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Thermodynamics of Sodium Carbonate in Solution

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THERMODYNAMICS OF SODIUM CARBONATE IN SOLUTION

A thesis submitted by

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INTRODUCTION AND PRESENTATION OF THE PROBLEM

An understanding of the behavior of electrolytes in solution is necessary for the elucidation of the kinetics and equilibria of many reactions. The utility of comprehensive thermodynamic data over a wide range of conditions is evident in many phases of the pulp and paper industry and in other industries. For instance, reliable data for solutions of electrolytes are needed for a better understanding of the pulping processes at elevated temperatures, the causticization of green liquor in the sulfate process, the bleaching of pulp with various chlorine compounds, the preparation of sulfite cooking liquors, and the proposed recovery methods for the neutral sulfite semichemical process.

In spite of the demand for such data, previous investigations have been limited to relatively few compounds over a narrow range of conditions. Comprehensive activity coefficient data above 60°C. have been determined only for sodium chloride and sulfuric acid. For such an important compound as sodium carbonate, activity coefficients have been reported only at 25°C. (1, 2). Similar data for a number of compounds used in the pulp and paper industry have not been determined.

Sodium carbonate is one of the chief inorganic raw materials used in industry. It has been estimated (3) that the total consumption of sodium carbonate in the United States was 4,474,000 tons in 1952. During the same year the pulp and paper industry utilized an estimated

305,000 tons. In addition, the continuous production of sodium carbonate in the recovery of the cooking liquors of the alkaline pulping process must be considered.

However, the study of sodium carbonate solutions is not important solely because of the extensive industrial use of sodium carbonate. From a scientific aspect, the study of the behavior of these solutions should yield valuable information for the calculations of chemical equilibria and reaction kinetics, estimation of the behavior of similar electrolytic solutions, and a number of other applications.

A program of research was therefore initiated to study the thermodynamics of sodium carbonate solutions with particular emphasis on the determination of the activity coefficient data. It was desirable to carry out experimental work over as wide a range of temperature and concentration as possible and thus obtain generally applicable data. Due to the limitations in the experimental methods of measuring thermodynamic data, two independent methods were chosen to cover the desired temperature range: (1) the measurement of the electromotive force of concentration cells from 15 to 65°C., and (2) the measurement of the vapor pressure of sodium carbonate solutions from 65 to 95°C. Comparison of the results at 65°C. derived from the two independent methods should yield additional information concerning the reliability of the thermodynamic data.

TABLE I

TABLE OF NOMENCLATURE

1. A bar over a quantity refers to a partial molal thermodynamic quantity.

2. A superscript zero refers to a value of a function in the standard state.

3. Subscripts refer to ionic or molecular constituents or to mean ionic quantities.

A - Debye-Hückel equation constant

a - activity

å - effective diameter of ions in Ångströms

B - Debye-Hückel equation constant

c - molarity in moles/1000 ml. of solution

D - dielectric constant

D - Logarithmic ratio of rational activity coefficients, Equations (57) to (60)

E - electromotive force

F - molal free energy

$\mathcal{F}$ - Faraday charge

f - rational activity coefficient

$\underline{f}$ - fugacity

H - molal enthalpy

H_D - molal heat of dilution

K - ionization constant; K_W-for water; K_{2A}-for 2nd constant of H_2CO_2

K_H - hydrolysis constant

TABLE I (CONTINUED)

k - Boltzmann constant

k_H-constant defined by Equation (77)

L - relative molal enthalpy

ln- logarithm to the base e

log - logarithm to the base 10

M - molecular weight

m - molality in moles 1000 grams solvent

N - mole fraction

N - number of Faraday equivalents

N - Avagadro number - Equation (50)

n - moles of gas

$\underline{P}$ - total pressure

P - vapor pressure

R - gas constant/mole

S_f- limiting slope of the Debye-Hückel equation

T - absolute temperature

x - degree of hydrolysis

z - valence

Γ - ional concentration

γ - molal activity coefficient

ε - electronic change

μ - ionic strength

ν - number of ions of an electrolyte

ρ - density

φ - osmotic coefficient

TABLE I (CONTINUED)

φ - function - Equation (61)

φ_L - apparent relative molal enthalpy

THEORY

Thermodynamics deals with systems in equilibrium, and the fundamental concepts of ideal gases and solutions are well established. However, real solutions approach the behavior of ideal solutions only in a very dilute state. To account for the nonideal behavior of solutions at ordinary concentrations, modifications of the fundamental functions have been devised, and the study of electrolytic solutions has become a very specialized field. Lewis and Randall (4) made a very important contribution to the thermodynamics of solutions by clearly outlining the concepts and correlating previous work on the basis of ionic properties. Recently, Harned and Owen (5) presented a very comprehensive treatise on this specific field. In the following sections are summarized the important principles relevant to the study of sodium carbonate solutions. The theory is based on the above mentioned references using the notations of Harned and Owen.

THERMODYNAMICS OF ELECTROLYTES IN SOLUTION

A consideration of some of the basic concepts of classical thermodynamics is necessary in the development of the theory of electrolytic solutions. The function of particular importance in chemical changes is the free energy. For a system undergoing a reversible change in state, at constant temperature and pressure, the free energy change is a measure of the net work available for external

utilization. Furthermore, Gibbs, (6) has demonstrated that, for a chemical reaction proceeding at constant temperature and pressure, a necessary criterion of equilibrium is that

$$(dF)_{P,T} = 0. \qquad (1)$$

This relationship has served as the basis of our understanding the complex equilibria of chemical reactions and processes.

The absolute values of F are not known; however, we are concerned only with the changes in free energy in passing from the initial to the final state. It is helpful to imagine the free energy as a chemical potential or a measure of the escaping tendency of a component in a system. However, it is desirable to introduce more restricted functions than free energy in studying solutions. In order to account for the nonideal behavior of solutions, Lewis introduced the fugacity ($\underline{f}$) and defined it by the equation

$$(dF = RT\ d\ (\ln \underline{f}) \qquad (2)$$

$$\Delta F = RT \ln \underline{f}/\underline{f}^{\circ} \qquad (3)$$

where R=gas constant per mole

T=absolute temperature

$\underline{f}^{\circ}$=fugacity at some arbitrary standard state

The definition of fugacity is not complete unless the standard state of the component of a system is established.

In dealing with multicomponent systems (e.g. a solution), it is convenient to use partial molal quantities. The partial molal free

energy ($\bar{F}_1$) of component (1) is defined by the equation

$$\bar{F}_1 \equiv (\partial F/\partial n_1)_{P,T,n2\ \cdots} \tag{4}$$

where F=the free engergy of the solution

$n_1, n_2 \cdots$=moles of components 1, 2...in solution

and Equation (4) becomes

$$\Delta F_1 = \bar{F}_1 - \bar{F}_1^\circ = RT \ln \underline{f}_1/\underline{f}_1^\circ \tag{5}$$

where $\bar{F}_1^\circ$ =partial molal free energy at the standard state

In many cases it is very difficult or impossible to determine the values of the fugacity for the components of a solution. However, the ratios of the fugacities may be determined, and Lewis introduced another thermodynamic property called the activity (a).

$$a \equiv \underline{f}/\underline{f}^\circ \tag{6}$$

Equation (5) becomes

$$\bar{F}_1 - \bar{F}_1^\circ = RT \ln a_1 \tag{7}$$

The concept of activity is particularly useful in dealing with liquid solutions. For example, if the standard state of a component in a solution is chosen as the pure component at the temperature and pressure of the solution, the activity becomes a function of the concentration of the component. For an ideal solution the activity is equal to the concentration of the component, and from Equation (7)

$$F_1 - F_1^o = RT \ln N_1 \qquad (8)$$

where N_1 = mole fraction of the component in solution $= n_1/n_1+n_2\cdots$

Thus, the activity provides a basis for the thermodynamic expression of concentration in terms directly related to the free energy.

The choice of standard states necessary to complete the definition of the fugacity and activity is arbitrary. However, it is desirable to select standard states which yield convenient scales related to the compositions of ideal solutions. The standard state of a liquid or a solid is taken customarily as the pure substance at a specified pressure, and the activity in the standard state is unity. For a solution, the standard state of the solvent is usually the pure substance at a specified pressure, while that of the solute is the state of infinite dilution at a specified pressure. It is not necessary for the component actually to exist in the standard state; the choice may be purely hypothetical.

For nonideal solutions, the activity of a component is not equal to the concentration as expressed in Equation (8). In working with solutions it is often convenient to think of the ratio of the activity to the concentration. Therefore, an empirical factor called the activity coefficient (f) is introduced and defined by the equation

$$f \equiv a/N \qquad (9)$$

In the preceding discussion we have been concerned with solutions in general. Let us now consider specifically electrolytic solutions. The thermodynamic functions apply strictly to the components of the solution, which were defined by Gibbs as the independently variable constituents. Thus, the solvent and the electrolytes are the only components of a solution. The ions are of fundamental importance in determining the behavior of the solution; however, the concentrations of the cations and anions are not independent variables and cannot be considered as components of the system. The thermodynamic functions are therefore developed in terms of hypothetical ionic activities. Only certain ionic activity products or ratios have any real physical significance.

Let us consider a binary solution consisting of a solvent and an electrolytic solute. For an electrolyte, $C_{\nu_+} A_{\nu_-}$, the dissociation into ions is represented by the equation

$$C_{\nu_+} A_{\nu_-} = \nu_+ C^{z+} + \nu_- A^{z-} \qquad (10)$$

where ν_+ = the number of cations per mole

ν_- = the number of anions per mole

$z+$ = valence of the cation

$z-$ = valence of the anion

The activity of the electrolyte in solution is expressed in terms of the activities of the individual ions and, by definition,

$$a \equiv a_{\pm}^{\nu} \equiv (a_{+}^{\nu_+} \; a_{-}^{\nu_-}) \tag{11}$$

where $\nu = \nu_+ + \nu_-$

a_+, a_- = activities of individual ions

$a_{\pm}$ = mean activity of the ions.

The use of the mean ionic activities permits the correlation of the properties of electrolytes of different valence types. For an electrolytic component of a solution, the partial molal free energy is given by the equation

$$\overline{F} - \overline{F}^{\circ} = RT \ln (a_{+}^{\nu_+} \; a_{-}^{\nu_-}) = \nu RT \ln a_{\pm} \tag{12}$$

The standard state of the solute is the dissociated electrolyte at infinite dilution, and the activity approaches the concentration as the concentration approaches zero. The standard state of the solvent is the pure substance at a pressure of one atmosphere.

For an ideal electrolytic solution, the free energy of a solute may be expressed by the equation

$$\overline{F}_2 - \overline{F}_2^{\circ} = \nu RT \ln N_{\pm} \tag{13}$$

where $N_{\pm}$ is the mean ionic mole fraction. The mean ionic mole fraction is defined by an expression analogous to that used for the mean ionic activity.

$$N_{\pm} \equiv (N_{+}^{\nu_+} \; N_{-}^{\nu_-})^{1/\nu} \tag{14}$$

In nonideal solutions the activity and concentration of the solute are not equal. From Equations (9), (11), and (14), the activity coefficient

is expressed by the equation

$$f_{\pm} = a_{\pm}/N_{\pm} = (f_{+}^{\nu_+} \; f_{-}^{\nu_-})^{1/\nu} \tag{15}$$

where $f_{\pm}$ = the rational activity coefficient

f_+, f_- = ionic mole fraction activity coefficients

From Equation (12), the basic equation for an electrolyte in solution is

$$\overline{F} = \overline{F}_N^{\circ} + \nu RT \ln f_{\pm} N_{\pm} \tag{16}$$

The partial molal free energy in the standard state has been written as $\overline{F}_N^{\circ}$ to indicate that the concentrations are expressed on a mole fraction basis.

In experimental work it is customary to express the concentration of the solute in terms of the molality (moles of solute per 1000 grams of solvent) and the following equations are applicable:

$$m_{\pm} \equiv (m_{+}^{\nu_+} \; m_{-}^{\nu_-}) = m(\nu_{+}^{\nu_+} \; \nu_{-}^{\nu_-})^{1/\nu} \tag{17}$$

where m = molality of the solute

m_+, m_- = molality of ionic constituents

$m_{\pm}$ = mean ionic molality

$$\gamma_{\pm} \equiv a_{\pm}/m_{\pm} = (\gamma_{+}^{\nu_+} \; \gamma_{-}^{\nu_-})^{1/\nu} \tag{18}$$

where $\gamma_{\pm}$ = practical activity coefficient or the mean ionic molal activity coefficient

γ_+, γ_- = ionic molal activity coefficients

$$\overline{F} = \overline{F}_m^{\circ} + \nu RT \ln (\gamma_{\pm} m_{\pm}) \tag{19}$$

Since the standard state of the solute is the dissociated ions at infinite dilution, the activity coefficient based on the different concentration scales are equal to unity at infinite dilution.

$$f_{\pm} = \gamma_{\pm} = 1 \tag{20}$$

It is necessary to obtain the relationship between $f_{\pm}$ and $\gamma_{\pm}$ at concentrations other than infinite dilution. By combining Equations (16) and (19)

$$\overline{F} = \overline{F}^{\circ}_{N} + \nu RT \ln (N_{\pm} f_{\pm}) = \overline{F}^{\circ}_{m} + \nu RT \ln (m_{\pm} \gamma_{\pm}) \tag{21}$$

At any solute concentration, m,

$$N_{\pm} = m_2/\nu\, m + 1000/M_1 \tag{22}$$

where M_1 = molecular weight of the solvent.

At infinite dilution, the limiting value of the ratio $N_{\pm}/m_{\pm}$ becomes

$$N_{\pm}/m_{\pm} = M_1/1000 \tag{23}$$

Substitution of this limiting ratio in Equation (21) yields

$$\overline{F}^{\circ}_{N} = \overline{F}^{\circ}_{n} + \nu RT \ln 1000/M_1 \tag{24}$$

By combining Equations (21) and (24)

$$\ln f_{\pm} = \ln \gamma_{\pm} + \ln [m_{\pm}/N_{\pm} (M_1/1000)] \tag{25}$$

Substitution of Equation (22) in (25) yields the relationship between $f_{\pm}$ and $\gamma_{\pm}$.

$$\ln f_{\pm} = \ln \gamma_{\pm} + \ln (1 + m\nu M_1/1000) \tag{26}$$

From a consideration of the chemical potentials of several components of a phase at constant temperature and pressure, the following

relationship, the Gibbs-Duhem equation, is obtained:

$$\sum_{1}^{o} N_i \, d \ln a_i = 0 \qquad (27)$$

This very important relationship permits the calculation of the activity of one component of a system when the activities of the other components are known.

In the special case where there are only two components consisting of a solvent and an electrolyte in solution, Equation (27) becomes

$$N_1 \, d \ln a_1 = -N_2 \, d \ln a_2 \qquad (28)$$

In many cases the activity of the solvent (a_1) may be determined from vapor pressure determinations, freezing point depression measurements, etc. Converting Equation (28) to a molality basis, the activity coefficient ($\gamma_{\pm}$) can then be derived from Equations (11) and (18) to yield:

$$1000/M_1 \, d \ln a_1 = - \nu m \, d \ln (m_{\pm} \gamma_{\pm}) \qquad (29)$$

$$d \ln \gamma_{\pm} = (-1000/\nu m M_i) \, d \ln a_1 - d \ln m_{\pm} \qquad (30)$$

With suitable data on a_1, the logarithmic ratio of activity coefficients at any two concentrations may be obtained by graphical integration of Equation (30).

The calculation of the activity coefficient ratios by graphical integration may be somewhat simplified by changing the form of Equation

(30). The osmotic coefficient (φ) is defined by the equation

$$\varphi = -1000/\nu m M_1 \ln a_1 \qquad (31)$$

By differentiating Equation (31) and substituting in Equation (30), and noting that d ln m = d ln $m_{\pm}$, the following equation results:

$$d \ln \gamma_{\pm} = -1/m \; d\,[m\,(1-\varphi)] \qquad (32)$$

When dm is changed to an equivalent form ($2m^{1/2}\, dm^{1/2}$) and Equation (32) is integrated between limits of m_2 and m_1.

$$\ln \gamma_{\pm 2}/\gamma_{\pm 1} = (\varphi_2 - \varphi_1) - 2\int_{m_1}^{m_2} (1-\varphi/m^{1/2})\, dm^{1/2} \qquad (33)$$

Equations (30) and (33) are not suitable for extrapolating the experimental data to infinite dilution; however, appropriate methods will be discussed in following sections.

It is important to consider some of the changes in the thermodynamic functions accompanying the variation of free energy or activity of the solute with temperature. By the Gibbs-Helmholtz equation

$$[d\,(\Delta F/T)/dT] = -\Delta H/T^2 \qquad (34)$$

where ΔH = enthalpy change.

By substituting Equation (20) in (34) and evaluating at constant composition

$$\overline{H}_2 - \overline{H}_2^{\circ} = -\nu RT^2(\partial \ln \gamma_{\pm}/\partial T) \qquad (35)$$

where $\overline{H}_2^{\circ}$ = the partial molal enthalpy of the solute at infinite dilution

For convenience, the relative partial molal enthalpy ($\bar{L}$) is introduced and defined by the equation

$$\bar{L} \equiv (\bar{H} - \bar{H}^{\circ}) \tag{36}$$

and

$$\bar{L}_2 = -\nu RT^2 \, (\partial \ln \gamma_{\pm} / \partial T) \tag{37}$$

$\bar{L}_2$ is therefore the enthalpy change of a solute from a reference state of infinite dilution to a given concentration. If accurate activity coefficient data for an electrolyte are available over a range of temperatures, Equation (37) may be used for determining $\bar{L}_2$.

Equation (34) could also be applied to activity data of the solvent. However, the change in the activity of the solvent with temperature is small, and usually the experimental data are not sufficiently accurate to calculate $\bar{L}_1$ for the solvent.

In order to obtain a better understanding of solution enthalpies, let us consider the enthalpies from a different point of view. The total enthalpy change of the solution from infinite dilution to any concentration is expressed as

$$L = n_1 \bar{L}_1 + n_2 \bar{L}_2 = n_2 \varphi_L \tag{38}$$

where φ_L = apparent relative molal enthalpy of the solution.

However, φ_L is equivalent to the integral heat of dilution (H_D) but of opposite sign.

$$\varphi_L = H_D \tag{39}$$

The integral heat of dilution data may be obtained from thermochemical measurements. Therefore, there is a second means of calculating the values of $\bar{L}_2$ by using the equation

$$\bar{L}_2 = -\Delta H_D - 1/2 m^{1/2} \left(\partial \Delta H_D / \partial m^{1/2}\right) \tag{40}$$

Equation (40) does not offer a satisfactory means of calculating ΔH_D from known values of $\bar{L}_2$.

The values of $\bar{L}_2$ are usually calculated from thermochemical data using Equation (40). The values of $\bar{L}_2$ calculated from Equation (37) are inherently less accurate than those calculated from Equation (40), but they are very useful in checking the consistency of activity coefficient data and valuable at temperatures where thermochemical measurements have not been made.

THERMODYNAMICS OF GALVANIC CELLS

A galvanic cell consists of two electrodes joined by an electrolytic solution. From the standpoint of chemical thermodynamics certain cells are very important because they yield a direct measure of the free energy change of the cell reaction under the proper conditions. For measurement of the free energy change, the following restrictions are necessary:

(1) the chemical reaction of the cell must be known and (2) the cell must be operated reversibly at constant temperature and pressure.

As a typical example, consider the cell

$$Ag\text{-}AgX \mid MX(m) \mid MHg$$

where M = an alkali metal

X = a halide

MHg = an alkali metal amalgam

The chemical reaction for this cell is

$$AgH\ (s) + M(s) = MX(m) + Ag(s)$$

where (s) refers to the compounds as solids. The change in free energy for the cell reaction is given by the equation

$$\Delta F = \Delta F^\circ + RT \ln [a\ (\text{products})/a\ (\text{reactants})] \quad (41)$$

where ΔF° = free energy change of reaction in standard state

When the cell is operated reversibly at constant temperature and pressure, the electromotive force of the cell (E) is related to the free energy change of the cell reaction by the equation

$$\Delta F = -N\mathcal{F}E \quad (42)$$

and

$$\Delta F^\circ = -N\mathcal{F}E^\circ \quad (43)$$

where N = the number of equivalents represented by the chemical reaction

$\mathcal{F}$ = Faraday charge

E° = standard e.m.f. of the cell with reactants and products in their standard states

Equation (41) therefore becomes

$$E = E^\circ - RT/N\mathcal{F} \ln [a\ (\text{products})/a\ (\text{reactants})] \quad (44)$$

From the choice of standard states outlined previously, AgX,M, and Ag have unit activity. The free energy change of the reaction therefore becomes a function of only the activity of the electrolyte MX at a concentration of m. From Equation (42) the electromotive force (e.m.f.) of the cell is given by the expression

$$E = E^{\circ} - \nu RT/N\mathcal{F} \ln (m_{\pm} \gamma_{\pm})_{MX} \qquad (45)$$

The only unknown values in Equation (43) are E° and $\gamma_{\pm}$. E° is evaluated by measuring the e.m.f. of the galvanic cell at various concentrations of MX and extrapolating the e.m.f. data to infinite dilution. Once E° has been determined the absolute values of the activity coefficient can be calculated at each concentration.

A second type of cell is a concentration cell with or without liquid junction. A concentration cell with liquid junction consists of two half-cells containing solutions of different concentration which are connected by a liquid junction. This cell is not used ordinarily in thermodynamic studies because of the difficulty in determining the liquid junction potential between the two half-cells. A concentration cell without liquid junction consists of two complete galvanic cells and may be represented as

$$Ag\text{-}AgX \mid MX(m_1) \mid MH_g \mid MX(m_2) \mid AgX\text{-}Ag$$

where m_1 and m_2 represent concentrations of the electrolyte. The net reaction of the cell is obtained by subtraction of the reaction of the first cell from that of the second cell. The net reaction therefore

represents the transfer of one mole of MX from concentration m_1 to m_2.

$$MX(m_1) = MX(m_2)$$

From Equations (41) to (45)

$$E = E_2 - E_1 = -RT/N\mathcal{F} \ln a_{\pm 2}^{\nu} / a_{\pm 1}^{\nu} = -\nu RT/N\mathcal{F} \ln m_{\pm 2} \gamma_{\pm 2} / m_{\pm 1} \gamma_{\pm 1} \quad (46)$$

The e.m.f. of a concentration cell therefore represents a measure of the free energy of dilution for any two concentrations, or more simply the e.m.f. is a measure of the ratio of the activity coefficients in the two solutions. It is customary to measure the e.m.f. of a series of concentration cells with m_1 constant and m_2 as a variable. The absolute value of the reference solution activity coefficient is calculated from a suitable form of the Debye-Hückel equation as discussed below and $\gamma_{\pm 2}$ values for all other solutions are calculated from Equation (46).

THE DEBYE-HÜCKEL THEORY

In 1923 Debye and Hückel (7) presented a theory to predict the behavior of strong electrolytes in dilute solution. The resulting Debye-Hückel equation provides a means of calculating the activity coefficients in dilute solutions. With certain modifications of the basic equation, the activity coefficients may be calculated over a much wider range of concentration. As mentioned previously, there are several experimental means of determining the ratios of the activity

coefficients of an electrolyte in solution at various concentrations. Thus the Debye-Hückel equation may be used to calculate the absolute value of the activity coefficient in a dilute solution, and the activity coefficients at higher concentrations are calculated from the ratios.

The theory is based on the statistical distribution of ions in solution (Boltzmann principle) and on the electrostatic attractive forces acting between the ions (Poisson equation). Since the theory has been adequately developed in numerous texts, only the major considerations are summarized in the following discussion.

The theory is developed from the concept that each ion is surrounded by an ionic atmosphere of opposite charge. Considering the ions as point charges the following equation is derived:

$$\log f_{\pm} = -S_f \sqrt{\Gamma} \qquad (47)$$

where S_f = the limiting slope of the Debye-Hückel equation

Γ' = the ional concentration

The ional concentration is defined in relation to the molar concentration of the ions.

$$\Gamma = \Sigma C_i Z_i^2 \qquad (48)$$

where c = molarity in moles per liter of solution.

The ional concentration is directly related to the more common ionic strength (μ) defined by Lewis and Randall as

$$\mu \equiv 1/2 \, \Sigma m_i \, Z_i^2 \tag{49}$$

The limiting slope, S_f, depends upon the valence type of the electrolyte and is defined for an electrolyte dissociating into p kinds of ions by the equation

$$S_f = 1/2{,}303\nu \sum_1^P \nu_i Z_i^2 \left[\pi N \varepsilon^6 / 1000(kDT)^3\right]^{1/2}$$

$$= 1/\nu \sum_1^P \nu_i z_i^2 \, (DT)^{-3/2} \, (1.283 \times 10^6) \tag{50}$$

where N = Avagadro number

ε = electronic charge

D = dielectric constant of solvent

k = Boltzmann constant

Thus, the limiting slope of the Debye-Hückel equation is specific for each type of electrolyte at a given temperature.

It is important to note that Γ is a function of the concentration of all the ions in the solution regardless of source, while the summation involved in S_f depends only upon the ions formed by the dissociation of the electrolyte to which $f_\pm$ refers. Equation (47) involves two concentration bases; $f_\pm$ is dependent on mole fractions, while Γ is dependent on molar concentrations. However, the product $S_f \sqrt{\Gamma}$

is dimensionless, and difficulties are thus avoided.

Let us consider the relationship between the activity coefficients of the individual ions of different valence at a given ional concentration. From Equation (50) the limiting slope is proportional to the square of the valence of the ion. If $f_{(2)}$ denotes the activity coefficient of an ion of valence z, the following relationship is obtained from Equation (47).

$$f_{(1)} = f_{-(2)}^{-1/4} = f_{(3)}^{1/9} \qquad (51)$$

Equation (51) is strictly applicable only in dilute solutions.

Let us next consider the relationships of the mean ionic activity coefficients for the various valence types. For an electrolyte that dissociates into two kinds of ions, the limiting slope is proportional to the product of the ionic valences $|z_+ z_-|$. If the activity coefficients are denoted as $f_\pm (z_+ z_-)$, the following relationship is obtained from Equation (47)*

$$f_\pm(1\text{-}1) = f_\pm^{1/2}(1\text{-}2) = f_\pm^{1/3}(1\text{-}3) = f_\pm^{1/4}(2\text{-}2) \cdots \qquad (52)$$

The simple form of the Debye-Huckel equation (47) and the above relationships are applicable only at concentrations where the size of

* See Figure 8 for graphical comparison of the limiting slopes for various valence types.

the ions is negligible in comparison to the distance between the ions. The validity of Equation (47) has been demonstrated up to an ional concentration of about 0.2. From Equation (26) $f_{\pm}$ and $\gamma_{\pm}$ are essentially equal over the applicable concentration range of Equation (47).

At higher concentrations the size of the ion must be taken into consideration and Equation (47) becomes

$$\log f_{\pm} = -S_f \sqrt{\Gamma}/1+A\sqrt{\Gamma} \qquad (53)$$

and

$$\log \gamma_{\pm} = -S_f\sqrt{\Gamma}/1+A\sqrt{\Gamma} - \log (1+\nu m M_1/1000) \qquad (54)$$

where A = a constant for each electrolyte at a given temperature

The constant A is a function of the effective diameter ($\mathring{a}$) of the ionic atmosphere or the distance of the closest approach of two ions expressed in Ångströms.

$$A = \mathring{a} \quad 35.57/(DT)^{1/2} \qquad (55)$$

Hückel considered the change in activity coefficient due to a change in the dielectric constant of the solvent. From the many complicated mathematical considerations, the following simple equation resulted:

$$\log f_{\pm} = -S_f\sqrt{\Gamma}/1 + A\sqrt{\Gamma} + Bc \qquad (56)$$

B is a constant for each electrolyte at a given temperature. The change in the dielectric constant is only one of the factors to be considered in concentrated solutions. It is better to consider the linear function Bc as empirical. From Equation (26) the practical activity coefficient is determined as

$$\log \gamma_{\pm} = -S_f\sqrt{\Gamma}/1 + A\sqrt{\Gamma} + Bc - \log (1+\nu m M_1/1000) \quad (57)$$

It is important to note that Equations (56) and (57) are applicable over a much wider range of concentration than the simpler forms of the Debye-Hückel equation. It should be noted that the original simple form of the equation is used for predicting activity coefficients at low concentrations, while the extended forms are used to fit experimental data at higher concentrations. These extended equations have been shown to fit activity coefficient data with high precision from low concentration to one molal for many electrolytes and even up to two molal in some cases.

In the development of the above forms of the Debye-Hückel theory, only the first two terms of the expansion of an exponential function were utilized. Subsequently, other extended forms of the equations have been developed. However, the contributions of the extended terms to the numerical value of the activity coefficients are significant only at relatively high concentrations. In most studies the utilization of the extended forms of the Debye-Hückel equation has not been justified because of the limited accuracy of the experimental data and the

complicated mathematical manipulations required.

APPLICATION OF THEORY TO SODIUM CARBONATE SOLUTIONS

It is necessary to establish the standard states of the components of the solutions. For the solvent, water, the standard state is chosen as the pure substance at a pressure of one atmosphere. For the solute, sodium carbonate, the standard state is chosen as the sodium and carbonate ions at infinite dilution. This standard state is hypothetical because in any solution of sodium carbonate, hydroxyl and bicarbonate ions are formed by hydrolysis. The experimental conditions are therefore chosen to minimize the errors in the thermodynamic data due to the hydrolysis of the salt.

In the calculation of the activity coefficient data, it is necessary to use a form of the Debye-Hückel equation [Equation (57)]. It is therefore assumed that the Debye-Hückel equation represents the behavior of sodium carbonate in solution from 0.1 to 1.0 m within the limits of experimental accuracy when constants A and B are accurately calculated. In light of the many successful applications of the theory to a wide variety of electrolytic solutions during the past 30 years (5), the assumption appears to be well-grounded.

In the remainder of this thesis the term "activity coefficient" refers to the mean ionic molal activity coefficient ($\gamma_{\pm}$) of the electrolyte in solution unless specifically noted otherwise.

Concentration Cells

By using concentration cells without liquid junction, described in a previous section, the activity coefficient ratios for sodium carbonate may be obtained. A cell is represented as

$$Ag\text{-}Ag_2CO_3 \mid Na_2CO_3(m_r) \mid NaHg \mid Na_2CO_3(m_2) \mid Ag_2CO_3\text{-}Ag$$

where m_r is a reference solution of constant composition used for all cell measurements and m_2 is varied. From Equation (46), the fundamental relationship for the concentration cell is

$$E = -3RT/2\mathcal{F} \ln (m_{\pm 2}\, \gamma_{\pm 2}/m_{\pm r}\, \gamma_{\pm r}) \qquad (58)$$

For preliminary considerations the effect of hydrolysis of the salt on the quantities in Equation (58) must be neglected. Measurements of the e.m.f. of a series of cells with increasing values of m yield the ratios of the activity coefficients of the solutions in respect to that of the reference solution. The Debye-Hückel equation is used to extrapolate the e.m.f. measurements to infinite dilution and determine the absolute values of the activity coefficients.

By substituting Equation (57) for $\log \gamma_{\pm}$ in Equation (58), the calculated e.m.f. E (calc.) for a given concentration is expressed as

$$E(\text{calc.}) = -(2.303)(3)RT/2\mathcal{F}\{\log m_{\pm 2}/m_{\pm r} + [-S_f\sqrt{\Gamma_2}/1+A\sqrt{\Gamma_2}(59) + Bc_2 - \log(1+0.054m_2)] - [-S_f\sqrt{\Gamma_r}/1+A\sqrt{\Gamma_r}+Bc_r - \log(1+0.054m_r)]\}$$

The method of Jones and Dole (8) provides a suitable means of evaluating A and B from a series of experimentally measured e.m.f. values.

Let the experimentally determined e.m.f. be represented by E (obs.) and

$$\Delta E = E\ (obs.) - E\ (calc.) \tag{60}$$

Examination of Equation (59) reveals that E (calc.) is a function (φ) of only A and B since Γ_2 and Γ_r are constants for each cell.

$$E\ (calc.) = \varphi\,(A,B) \tag{61}$$

By partial differentiation of Equation (61), and the use of finite differences,

$$\Delta E = [\partial\varphi/\partial A]\ \Delta A + [\partial\varphi/\partial B]\ \Delta B \tag{62}$$

By carrying out the partial differentiation of Equation (59) in accordance with Equation (62),

$$\Delta E = -(2.303)(3)RT/2\mathcal{F}\left\{[S_f\sqrt{\Gamma_2}/(1+A\sqrt{\Gamma_2})^2 - S_f\sqrt{\Gamma_r}/(1+A\sqrt{\Gamma_r})^2]\Delta A + (c_2-c_r)\ \Delta B\right\} \tag{63}$$

By combining Equations (60) and (63), an equation suitable for determining average values of A and B is obtained. The corrected values of the constants are given by the equations

$$A' = A + \Delta A \tag{64}$$

and

$$B' = B + \Delta B \tag{65}$$

The following procedure is then used. By assuming reasonable values for A and B, Equation (59) is evaluated for each concentration cell. The values of ΔE are then obtained from Equation (60). The numerical factors for ΔA and ΔB in Equation (63) are calculated,

and ΔA and ΔB are solved by the method of least squares or similtaneous equations derived by separating the family of equations into two groups. With the new values of A and B from Equations (64) and (65), the above process is repeated until ΔA, ΔB, and ΔE are negligible.

The values of A and B determined by the above procedure are substituted in Equation (57) and the absolute value of the activity coefficient of the reference solution is evaluated.

$$\log \gamma_{\pm} = -S_f \sqrt{\Gamma_r} / (1 + A\sqrt{\Gamma}) + Bc_r - \log(1+0.054m_r) \quad (66)$$

Finally the activity coefficients ($\gamma_{\pm 2}$) of all the solutions used in the concentration cells are calculated from Equation (58), the fundamental equation for the cells.

When sodium carbonate is dissolved in water, sodium and carbonate ions are formed

$$Na_2CO_3 \overset{H_2O}{=\!=} 2Na^+ + CO_3^=$$

Due to hydrolysis of this salt, a portion of the carbonate ions are in equilibrium with bicarbonate and hydroxy ions.

$$CO_3^= + H_2O = HCO_3^- + OH^-$$

Because of this hydrolysis, the analytically determined value of m cannot be used in determining $m_{\pm}$ by Equation (18)

$$m_{\pm} + m (\nu_+^{\nu_+} \nu_-^{\nu_-})^{1/\nu} \quad (18)$$

It is necessary to use an equivalent form of Equation (18) to calculate $m_{\pm}$

$$m_{\pm} = \left\{(\nu_+ m)^{\nu_+} [\nu_- m(1-x)]^{\nu_-}\right\}^{1/\nu} \qquad (68)$$

where x = the hydrolyzed fraction of the carbonate ion concentration or the degree of hydrolysis.

However, the degree of hydrolysis x can be determined only from reliable activity data for the ionic constituents of the solution.

As stated previously, the experimental program must be designed to minimize the errors due to hydrolysis. In previous studies on electrolytes, experimental measurements have been extended to low concentrations so that the extrapolation of the experimental data to infinite dilution is required only over a very small concentration range. However, for sodium carbonate solutions, the errors caused by hydrolysis increase as the concentration decreases. For determining the absolute values of the activity coefficients, it is therefore preferable to make experimental measurements only at 0.1 m and above and to rely upon the Debye-Hückel equation for extrapolation of the data to the standard state of the nonhydralized sodium carbonate at infinite dilution.

The following method of calculation is adopted. As a first approximation, the activity coefficients are calculated using Equations (58) to (67) and neglecting the effect of hydrolysis. Subsequently, the corrected values of $m_{\pm}$ are calculated from the activity coefficient data.

The process is repeated until the changes in the values of $m_{\pm}$ and $\gamma_{\pm}$ are negligible.

The corrections necessary for the hydrolysis of the salt are derived at constant temperature and concentration. From Equation (51)

$$\gamma_{Na^+} \cong \gamma_{CO_3^=}^{1/4} \tag{69}$$

From Equation (19)

$$\gamma_{\pm} = (\gamma_{Na^+}^{2} \gamma_{CO_3^=})^{1/3} \cong (\gamma_{Na^+}^{2} \gamma_{Na^+}^{4})^{1/3} \cong \gamma_{Na^+}^{2} \tag{70}$$

and

$$\gamma_{\pm} \cong \gamma_{CO_3^=}^{1/2} \tag{71}$$

Thus, $\gamma_{CO_3^=}$ and γ_{Na^+} may be calculated approximately from $\gamma_{\pm}$. In the mixture of ions produced by hydrolysis, the activity coefficients of the univalent ions are assumed to be approximately equal.

$$\gamma_{Na^+} \cong \gamma_{HCO_3^-} \cong \gamma_{OH^-} \tag{72}$$

It is now possible to express the hydrolysis constant K_H in terms of the activities of the ions if the concentration of the carbonate ions is m.

$$CO_3^= + H_2O = HCO_3^- + OH^-$$

$$m(1-x)\gamma_{CO_3^=} \quad a_{H_2O} \quad mx\gamma_{HCO_3^-} \quad mx\gamma_{OH^-}$$

$$K_H = a_{HCO_3^-} a_{OH^-} / a_{CO_3^=} a_{H_2O} = (mx\gamma_{HCO_3^-})(mx\gamma_{OH^-}) / [m(1-x)\gamma_{CO_3^=}](a_{H_2O}) \tag{73}$$

The value of K_H may be determined by introducing the ionization constant of water, K_W, and the second ionization constant of carbonic acid, K_{2A}.

$$H_2O = H^+ + OH^-$$

$$a_{H_2O} \quad a_{H^+} \; a_{OH^-}$$

$$K_W = a_{H^+} \; a_{OH^-}/a_{H_2O} \tag{74}$$

and

$$HCO_3^- = CO_3^= + H^+$$

$$a_{HCO_3^-} \; a_{CO_3^=} \quad a_{H^+}$$

$$K_{2A} = a_{CO_3^=} \; a_{H^+}/a_{HCO_3^-} \tag{75}$$

By taking the ratio of K_W to K_{2A}

$$K_W/K_{2A} = [(\cancel{a_{H^+}})(a_{OH^-})/(a_{H_2O})]/[(a_{CO_3^=})(\cancel{a_{H^+}})/(a_{HCO_3^-})] = (a_{HCO_3^-})(a_{OH^-})/$$

$$(a_{CO_3^=})(a_{H_2O}) = K_H \tag{76}$$

Thus the numerical value of K_H may be determined at temperatures where K_W and K_{2A} are known.

In order to simplify notation let

$$k_H \equiv K_H \; (\gamma_{CO_3^=}/\gamma_{HCO_3^-} \; \gamma_{OH^-}) = m \; x^2/(1-x) \tag{77}$$

The quantity k_H is a variable and must be determined for each concentration. The degree of hydrolysis may be determined by solving Equation (77) for x.

$$x = -k_H/2m + \sqrt{(k_H/2m)^2 + k_H/m} \qquad (78)$$

For each concentration of sodium carbonate used in the concentration cells, the degree of hydrolysis is calculated using Equation (70) to (72) and (76) to (78). Finally the corrected value of $m_{\pm}$ are calculated using Equation (68).

Consider Equation (58) again. If the errors in the ratio $m_{\pm 2}/m_{\pm r}$ due to using the approximate values of $m_{\pm}$ instead of the corrected values from Equation (68) are appreciable, the entire process of calculating the activity coefficients is repeated until the changes in $m_{\pm}$ and $\gamma_{\pm}$ are negligible. As will be shown subsequently, the errors due to hydrolysis were small because of the experimental conditions and successive approximations were not necessary

The Vapor Pressure of Solutions

In the gas saturation method of determining the vapor pressure of a solution in comparison with that of water at the same temperature, n_o moles of dry nitrogen are passed first through a system containing pure water and then through a system containing the solution. In the water system at a total pressure of P, the nitrogen absorbs n moles of

water vapor until the gas phase is at equilibrium saturation according to Dalton's law.

$$P = n/n + n_o \quad \underline{P} \tag{79}$$

where P = vapor pressure of water at a given temperature. In the solution system at a total pressure of $\underline{P}_1$, the nitrogen absorbs n_1 moles of water vapor at equilibrium saturation, and

$$P_1 = n_1/n_1 + n_o \quad \underline{P}_1 \tag{80}$$

By eliminating n_o from Equations (79) and (80), the vapor pressure of the solution is given by the equation

$$P_1 = n_1 \underline{P}_1 P / n(\underline{P} - P) + n_1 P \tag{81}$$

Since water vapor approaches the behavior of an ideal gas over the temperature range of this investigation, the activity of the water (a_1) in a solution is given as the ratio of the vapor pressure of the solution to that of pure water.

$$a_1 = \underline{f}/\underline{f}^{\circ} = P_1/P \tag{82}$$

When the vapor pressures of a series of solutions are measured at constant temperature, the logarithmic ratios of the activity coefficients may be obtained from Equation (33) or by integration of Equation (30)

$$\log \gamma_{\pm 2}/\gamma_{\pm r} = -\int_{a_1 \text{ at } m_r}^{a_1 \text{ at } m_2} 18.502/m \; d \log a_1 - \log m_2/m_r \qquad (83)$$

$$\ln \gamma_{\pm 2}/\gamma_{\pm r} = (\varphi_2 - \varphi_1) - 2\int_{m_r}^{m_2} (1 - \varphi/m^{1/2}) \, dm^{1/2} \qquad (33)$$

A method of extrapolating the data to infinite dilution similar to that used for the concentration cells may be developed to yield comparable results. A few simplifications in form are employed to reduce the mathematical procedures. The data obtained from Equation (83) or (33) are converted to the mole fraction basis by Equation (26) and abbreviated

$$D = \log f_{\pm 2}/f_{\pm r} \qquad (84)$$

Let $$\Delta D = D - D \text{ (calc)} \qquad (85)$$

and $$D \text{ (calc.)} = -S_f\sqrt{\sqrt{2}}/1+A\sqrt{\sqrt{2}} + Bc_2) - (-S_f\sqrt{\sqrt{r}}/1+A\sqrt{\sqrt{r}} + Bc_r) \qquad (86)$$

$$\Delta D = [S_f \sqrt{2}/(1+A\sqrt{\sqrt{}})^2 - S_f \sqrt{r}/(1+A\sqrt{\sqrt{r}})^2] \; \Delta A + (C_2 - C_r) \; \Delta B \qquad (87)$$

$$A' = A + \Delta A \qquad (88)$$

$$B' = B + \Delta B \qquad (89)$$

Using Equations (84) through (89) and the procedure outlined for concentration cell data, A and B are determined. $\gamma_{\pm r}$ is calculated from Equation (67), and $\gamma_{\pm 2}$ values are calculated from the results from Equation (83) or (33).

In the method just outlined for calculating the activity coefficients, certain limitations or sources of error should be pointed out. It is assumed that the solutions contain only a single solute which is sodium carbonate. Strictly speaking, the solutions consist of a mixture of sodium carbonate, hydroxide, and bicarbonate as mentioned previously. From the Gibbs-Duhem equation (27)

$$N_1 \, d \ln a_1 = -N_{Na_2CO_3} \, d \ln a_{Na_2CO_3} - N_{Na\,HCO_3} \, d \ln a_{NaHCO_3}$$

$$- N_{NaOH} \, d \ln a_{NaOH} \cong -N_2 \, d \ln a_2 \qquad (90)$$

where N_2 = apparent mole fraction of sodium carbonate

a_2 = apparent activity of sodium carbonate

At low concentrations Equation (90) does not apply because of the high degree of hydrolysis. However, if the equation is applied only at 0.1 m and above, the errors in calculation are minimized.

PREVIOUS WORK ON SODIUM CARBONATE SOLUTIONS

In 1939 Lortie and Demers (1) calculated the activity coefficients at 25°C. from 0.005 to 1.852 m from data reported in the literature on freezing point depression measurements and vapor pressures of solutions. On the basis of the Gibbs-Duhem equation, they developed a theory for dealing with hydrolyzed salts. Corrections were made for the effect of hydrolysis on sodium carbonate concentrations. However, they used the approximation indicated in Equation (90) which is not accurate at

0.005 m. Realizing this difficulty, they graphically extrapolated the data to infinite dilution rather than using the Debye-Hückel equation. The value of the activity coefficient calculated at 0.005 m was actually a function of the activity coefficients of sodium carbonate, bicarbonate, and hydroxide. By making a number of approximations, the authors estimated that the calculated activity coefficients over the entire concentration range were consistently 2.6 to 3.1% high due to the errors in the activity coefficient at 0.005 m. Another possible source of error in their calculations was the conversion of the activity coefficient data from the freezing points of the solutions to 25°C. Lortie and Demers realized the errors involved in their calculations, but concluded that there was no way to compensate accurately for effects of hydrolysis in determining the absolute values of the activity coefficients. However, the ratios of the activity coefficients at various concentrations should be as accurate as the original experimental data.

Saegusa (2) recently calculated the activity coefficients of sodium carbonate in solution at 25°C. from 0.001 to 2.7 m. He measured the e.m.f. of the galvanic cell

$$NaHg \mid Na_2CO_3(m) \mid Ag_2CO_3 - Ag$$

There are several inaccuracies in the calculations of the activity coefficient data. In correcting for the effect of hydrolysis on the

values of $m_{\pm}$, Saegusa calculated the degree of hydrolysis. In Equation (77) he assumed that the ratio of the ionic activity coefficients was equal to unity at each concentration.

$$(\gamma_{HCO_3^-}\ \gamma_{OH^-}/\gamma_{CO_3^=}) = 1$$

However, the assumption is valid only for dilute solutions and appreciable errors result over most of the concentration range. Equation (45) applies to the cells, and the value of E° must be determined. Saegusa determined E° by plotting the experimental e.m.f. values as a function of the square root of the ionic strength [Equation (49)] and extrapolating the curve to infinite dilution. This type of extrapolation is not very satisfactory because it exhibits curvature at the lowest concentrations, and too much weight must be given to the most dilute solutions where the measurements are least trustworthy. Previous studies have indicated that the reliability of the sodium amalgam electrode is questionable below 0.05 m (9). In addition, silver carbonate is sufficiently soluble so that its concentration is significant in the dilute sodium carbonate solutions. It is not possible to estimate the magnitude of the errors in extrapolation caused by the above factors. However, it appears that more accurate activity coefficients could be calculated from the e.m.f. data of Saegusa if some form of the Debye-Hückel equation were employed.

Unfortunately very little work has been done concerning the thermochemistry of sodium carbonate solutions. On the basis of meager experimental data reported by Thomsen in 1871, Watson and Kowalke (10) calculated the relative partial molal enthalpies and specific heats at 18°C. Extrapolation of the data from about 0.2 m to infinite dilution was accomplished by a graphical technique. No corrections were made for the change in the sign of the heat of dilution when the concentration approaches infinite dilution or for the heat effects due to hydrolysis of the salt, which may be appreciable.

Bichowsky and Rossini (11) reported the enthalpies of sodium carbonate solutions from infinite dilution to 3.7 m at 18° C. The data were based on the measurements of Thomsen and two other investigators. The values below 0.28 m were estimated. The authors state that the results are consistent with those reported for other compounds in their monograph, but no details are given on the method of extrapolation or corrections included for heat effects of hydrolysis.

Kobe and Sheehy (12) surveyed the literature concerning the thermochemistry of sodium carbonate including solubilities, heats of solution (from Bichowsky and Rossini), specific heats of the salt and solution, and heats of decomposition. It does not appear that sufficient data of reliable accuracy are available to calculate the relative partial quantities of the solutions from thermochemical data.

DETERMINATIONS OF THE ELECTROMOTIVE FORCES OF CONCENTRATION CELLS

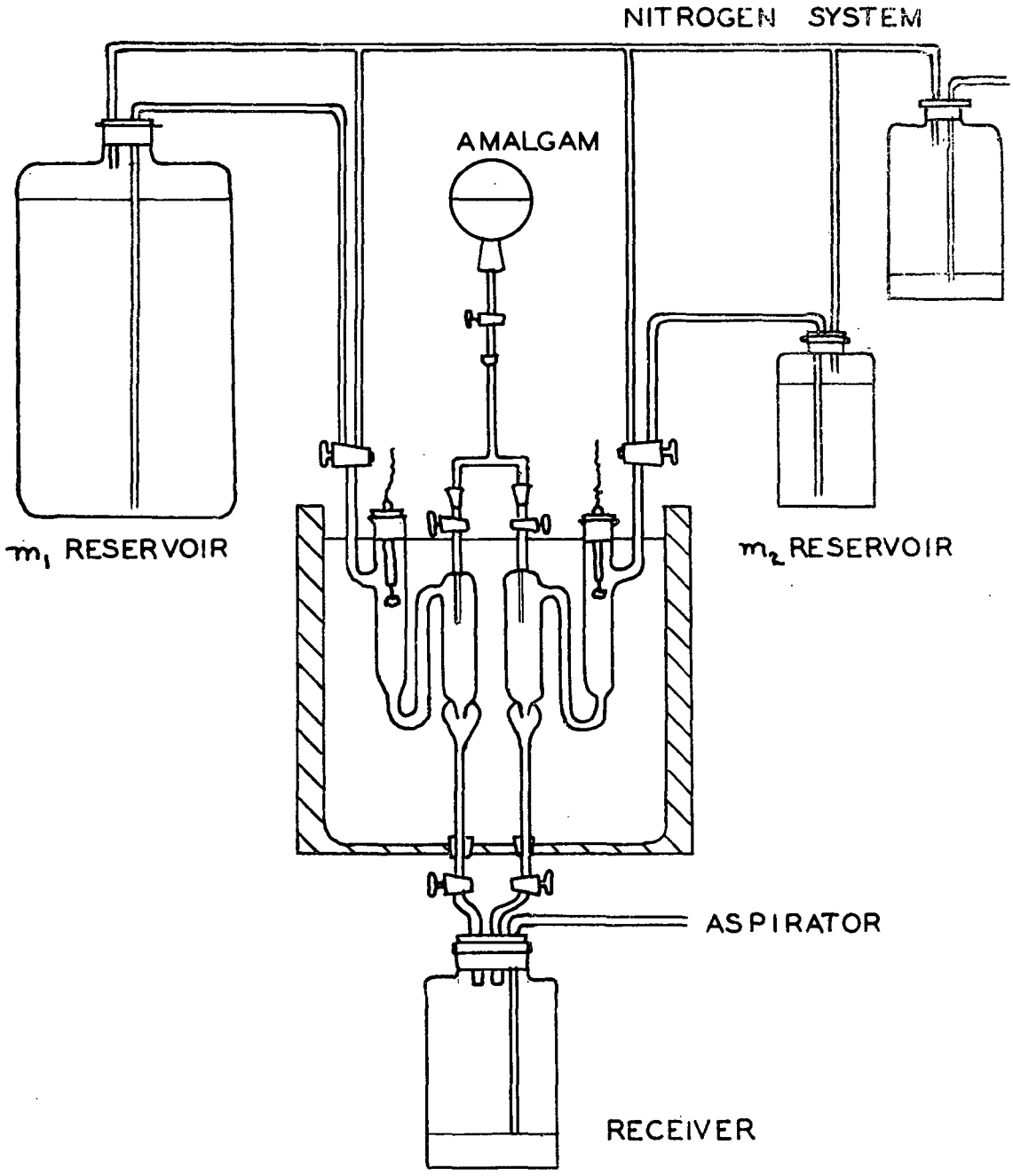
APPARATUS

A concentration cell consists of two component cells containing separate solutions, silver-silver carbonate electrodes, and capillary droppers filled with sodium amalgam. The two component cells are connected to a common amalgam reservoir. An electrical connection between the cells exists only when amalgam is flowing from the reservoir into both cells. A concentration cell, similar in principle to those used in previous studies, was made of Pyrex glass and mounted in a thermostat as shown in Figure 1.

The concentration cell was connected to the solution and amalgam reservoirs above and to the receiver flask below. The entire apparatus was connected to a nitrogen supply system maintained at a positive pressure of 1/2 inch of mercury to exclude oxygen from the solutions at all times. With the exception of the reference solution reservoir, Pyrex glassware was used throughout the apparatus to keep the attack of the solutions on the glass to a minimum. The reference solution reservoir, m_1 reservoir in Figure 1, was a 5-gallon bottle containing 0.1 m sodium carbonate solution used in all cell measurements. The bottle was lined with a polyethylene plastic bag to keep the solution from contacting the soft glass. The second solution reservoir of 1-liter

FIGURE 1

CONCENTRATION CELL APPARATUS



capacity, m_2 reservoir in Figure 1, held the sodium carbonate solutions which were varied from 0.01 to 2.5 m in the first series of experiments. The amalgam reservoir was an inverted 1-liter flask connected to the cells through a spherical ground-glass joint for flexibility. A receiver flask below the thermostat was connected to both the cell units individually and to an aspirator. The arrangement of the equipment provided a simple means of filling and emptying the cell units, collecting the amalgam from the cells, and changing the concentration of the solution in the second cell unit.

The thermostat was a large battery jar supported on a stand 12 inches above the bench. Through the bottom of the jar two holes were cut for connecting the cell units and the receiver. The jar was insulated with an inch layer of hair felt covered with asbestos sheeting and filled with sufficient water to cover the cells. The temperature was controlled by a mercury-to-platinum thermoregulator operating a 200-watt intermittent heater through a relay. The maximum cyclical fluctuation in the bath temperature was 0.01°C. as measured with a Beckmann thermometer. Using a thermometer calibrated by the Bureau of Standards, the thermoregulators were set to $\pm$ 0.02°C. of the desired temperatures . When the thermostat was operated at temperatures above 25°C., a layer of liquid paraffin on top of the water prevented evaporation and permitted sensitive temperature control. Below or slightly above room temperature cooling water was run through copper coils in the bottom of the bath.

The e.m.f. values of the concentration cells were measured with a Leeds and Northrup Type K potentiometer and a Rubicon high-sensitivity galvanometer. A 2-volt cell of an ordinary storage battery was used as a working potential. The potentiometer was periodically standardized by comparing the reference cell and an Epply Standard Cell (1.01884 international volts at 24°C.).

SODIUM CARBONATE SOLUTIONS

Analytical grade anhydrous sodium carbonate was used for the preparation of all solutions. The purity of the salt as determined with constant-boiling hydrochloric acid diluted to 0.5000 M (13) was 99.8 to 99.9% after heating in an oven at 140°C. for one hour. The solutions were prepared using weighed amounts of sodium carbonate and twice-distilled water. Since dissolved oxygen had an adverse effect upon the potential of the sodium electrode, the solutions were poured into the 1-liter bottle used as the solution reservoir, and an aspirator was connected to the bottle. Water-pumped nitrogen was bubbled through the solution for about ten minutes to strip out all the oxygen. The reservoir was then attached to the apparatus and the nitrogen supply system. For the 0.1 m reference solution, 18 liters were prepared in the large reservoir, and nitrogen was bubbled through the solution for about an hour.

For the analysis of a solution, samples were pipetted into tared, glass-stoppered Erlenmeyer flasks, weighed, and titrated to the methyl orange end point with standard hydrochloric acid. Analyses were run in triplicate.

SODIUM AMALGAM PREPARATION

The amalgam containing 0.2% sodium was prepared by electrolysis with a sodium hydroxide solution over reagent grade mercury. The apparatus is shown in Figure 2. Approximately 4500 to 5000 grams of amalgam were prepared at one time.

A portion of the mercury was transferredto the electrolysis cell and covered with a solution of 25 grams of sodium hydroxide. A current of about 2 amperes was passed through the cell until the calculated amount of sodium was formed. After the sodium hydroxide solution was removed by decantation, the amalgam was washed successively three times with water and three times with acetone. Under a stream of nitrogen the amalgam was passed through a small hole in a filter paper into the reservoir containing the remainder of the mercury. The reservoir was connected to a vacuum pump, and the amalgam was allowed to dry overnight. Dry nitrogen at a pressure slightly above atmospheric was introduced into the reservoir. The reservoir was then inverted and connected to the concentration cell. Using this procedure, only a very thin film

FIGURE 2
AMALGAM ELECTROLYSIS

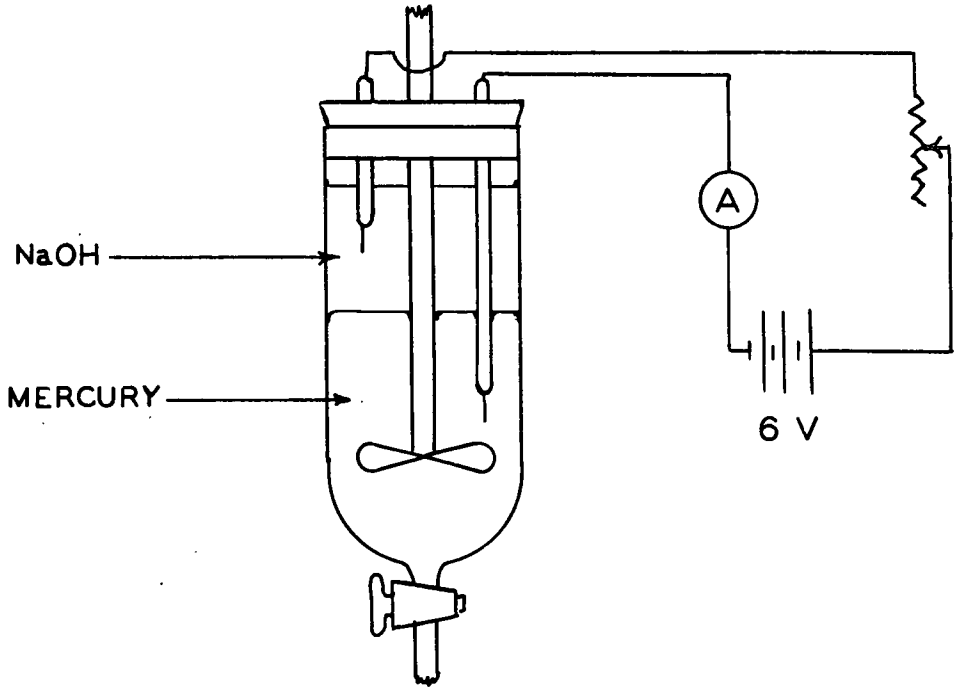
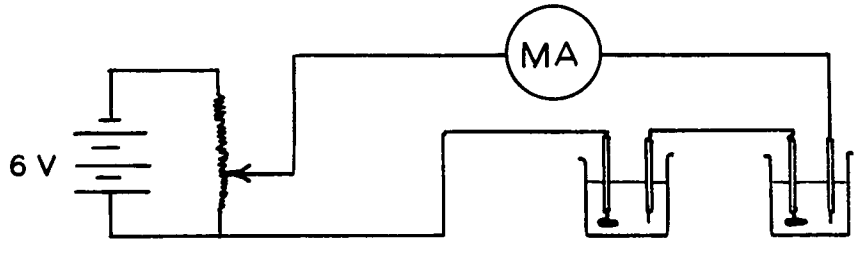


FIGURE 3
ELECTRODE ELECTROLYSIS



of sodium hydroxide or sodium oxide was formed on the surface of the amalgam and was later deposited on the walls of the reservoir.

During the operation of the cells the amalgam came into contact with only the sodium carbonate solutions and distilled water. It did not appear to be necessary to redistill the mercury before using it again in the amalgam. However, the mercury was cleaned by passing it in a fine spray successively through a 25% nitric acid solution and then through distilled water.

PREPARATION OF SILVER-SILVER CARBONATE ELECTRODES

The electrodes used in this research were Type 2 electrodes described by Harned (14). A platinum wire was sealed in a soft glass tube, the end of the wire was bent into a flat spiral, and a spongy mass of silver was formed on the spiral by decomposition of silver oxide. The silver carbonate was formed by electrolysis in a sodium bicarbonate solution (15) as shown in Figure 3.

Considerable difficulties were encountered in making reproducible electrodes. A number of the first electrodes made were erratic, and potential differences up to 5 mv. were recorded after the electrodes had been in the same solution for several hours. One of the major difficulties was inadequate cleaning of the platinum wires. Cleaning the platinum in boiling nitric acid and flaming to a red heat were

insufficient to produce wires of equal potential in the salt solutions. Mechanical abrasion with emery cloth was necessary to produce wires of equal and constant potential.

The silver oxide was formed by mixing equal molar quantities of silver nitrate and sodium hydroxide. After a thorough washing with distilled water, a thin paste of the oxide was put on the platinum spirals. The electrodes were placed in an oven at 450°C. until all the oxide had decomposed. Additional coatings of oxide were applied and decomposed until a uniform layer of spongy silver surrounded the platinum wires. The behavior of the electrodes depended upon the porosity of the spongy silver. For the preliminary work at 25°C., electrodes with a fine porous structure were prepared using silver oxide precipitated from concentrated silver nitrate solutions. In subsequent work, in an attempt to speed equilibration time, electrodes with large pores were formed from silver oxide precipitated from a dilute solution. When these electrodes were placed in the concentration cell, equilibrium conditions could not be reached, and the measured e.m.f. continually drifted to lower values. Therefore, electrodes of fine porosity silver were used for all cell measurements.

The first electrodes were electrolyzed in a 0.5 m sodium bicarbonate solution at a current density of 20 ma./cm.^{3} of electrode for a period of 30 minutes (15). These conditions are comparable to those used for silver-silver chloride electrodes. The potential

difference between two of the electrodes in a solution was usually less than a millivolt shortly after preparation, but the electrodes soon became erratic. The solubility of silver carbonate is considerably higher than that of silver chloride. The amount of silver carbonate on the electrode was therefore increased by raising the current density to 200 ma./cm.^{3} for two hours. The resulting electrodes gave the same initial potential as the previous electrodes, but the readings remained constant. As a standard practice, a pair of electrodes was electrolyzed in series at a current of 5 ma.(or about 200 ma.cm.^{3} of electrode) for two hours. With care in each step of the preparation, most of the electrodes were reproducible within 0.1 mv.

FILLING AND OPERATING THE CONCENTRATION CELLS

A special technique was developed for filling the cells with solution and maintaining the amalgam column between the cell units. Solution was drawn back into the amalgam tubes unless great care was exercised. The presence of moisture in the amalgam tubes resulted in the evolution of hydrogen and the separation of the amalgam at the stopcock or directly above the capillary droppers.

After two electrodes were put in the cells, both cell units and the receiver were evacuated by means of aspirator. Solution remaining in the cells was drawn out. The amalgam column broke at a point just above the capillary droppers, and amalgam was drawn from

the droppers. The cells were flushed with nitrogen to remove traces of oxygen. After the system was again evacuated, the stopcock on a cell unit below the thermostat was closed. The cell was filled by first turning on the amalgam stopcock to fill the dropper and then turning on the solution stopcock. When the solution completely filled the cell, the amalgam was turned off. The same procedure was used to fill the second cell. The aspirator was turned off, and the receiver was relieved to atmospheric pressure. The cell units were successfully filled at any of the operating temperatures of the thermostat.

For the work at 25°C., the electromotive force of each concentration cell was measured periodically until the equilibrium value was reached. During the readings the amalgam flowed in a steady stream into each cell unit and provided an electrical connection between the units. While the amalgam was flowing, the stopcocks between the solution reservoirs and the cell units were opened to provide an outlet for the solution displaced by the amalgam. The amalgam collected in the bottom of the cell units was drawn off into the receiver after each reading. During the course of the investigation, it was found that solution must flow through the cells during the equilibration time to yield reproducible results. A flow rate of 1/2 to 1 ml. per minute was sufficient. The e.m.f. of concentration cells from 0.01 to 2.5 m were measured at 25°C.

After the preliminary work at 25°C. was completed, the e.m.f. of the concentration cells was measured at 15, 25, 37, 5, 50, and 65°C. The reference solution was maintained at 0.1 m, and the variable solutions were 0.2, 0.4, 0.6, 0.8, 1.0, and 1.5 m.

Several procedures were tested in the measurement of the e.m.f. of a given concentration cell at the various temperatures. At the higher temperatures the rate of diffusion of the solutions increases, and the electrodes presumably come to equilibrium in a shorter time. However, it was found that the electrodes were somewhat unstable above 50°C. and irreversible changes occurred after extended periods at 50°C. and above. The instability of the electrodes was probably partially due to the increased solubility of the silver carbonate at the higher temperatures and sodium carbonate concentrations. The most reliable procedure was to allow the concentration cell to come to equilibrium at 25°C. Once the electrodes were in equilibrium with the solutions at 25°C., they rapidly came to equilibrium when the temperature of the bath was changed. The e.m.f. of the cell was next measured at 15°C. and subsequently measured at each temperature up to 65°C. Above 25°C. the cells reached temperature equilibrium after about 10 minutes at controlled temperature and readings were essentially constant. The temperature of the bath was rapidly changed by siphoning out the water and refilling with hotter or colder water. Fresh solution was passed through the cell units at a low rate except for a five-minute period before each e.m.f. measurement was made.

RESULTS AT 25°C.

The equilibrium e.m.f. of the concentration cells

$$Ag\text{-}Ag_2CO_3 \mid Na_2CO_3(0.1) \mid NaHg \mid Na_2CO_3(m_2) \mid Ag_2CO_3\text{-}Ag$$

are listed in Table II. For each solution, two or three pairs of electrodes were used to measure the e.m.f. The precision of the measurements is indicated by comparing the results from the different pairs of electrodes at the same concentration. The sign of the e.m.f. is indicated in relation to the reference solution electrode at zero potential.

When this research was undertaken it was assumed that the e.m.f. of each cell unit was a true measure of the reversible reaction

$$2Ag+Na_2CO_3(m) = Ag_2CO_3+2Na(NaxHg)$$

and that the over-all reaction of the concentration cell represented the transfer of one mole of sodium carbonate from concentration m_r to m_2

$$Na_2CO_3(m_r) = Na_2CO_3(m_2).$$

The validity of this assumption was established by calculating the e.m.f. of a series of concentration cells from activity coefficient data reported in the literature and comparing them with the values listed in Table II.

TABLE II

ELECTROMOTIVE FORCES OF CONCENTRATION CELLS AT 25°C.

E.m.f. Readings in mv.*

Molality	1	2	3	average
0.0102	71.26	72.31	71.59	71.69
0.0475	22.25	22.47	22.49	22.40
0.1007	reference solution			0.00
0.2004	-20.19	-20.34	-	-20.26
0.4039	-40.46	-40.53	-40.62	-40.54
0.6130	-52.83	-52.40	-	-52.61
0.8060	-60.60	-60.94	-	-60.77
0.9991	-66.53	-66.87	-	-66.70
1.5139	-78.70	-78.63	-	-78.66
2.009	-86.54	-86.60	-	-86.57
2.510	-91.62	-92.14	-	-91.88

*E.m.f. measured in relation to the reference solution electrode at zero potential

Activity coefficient data for sodium carbonate derived from freezing point and vapor pressure measurements were reported by Lortie and Demers (1). Since these data were derived from a different experiment technique for measuring free energy changes the electromotive force values calculated from the fundamental Equation (58) are true measures of reversible reactions.

$$E \text{ (calculated)} = -3RT/2\mathcal{F} \ln (m_{\pm 2} \gamma_{\pm 2}/m_{\pm r} \gamma_{\pm r})$$

For a comparable basis, the reference condition was selected at 0.1 m and activity coefficient of 0.480. The experimental e.m.f. (E observed) were measured in reference to a solution of 0.1007 m and read from a smooth curve of the data in Table II. The results of the calculations are shown in Table III.

TABLE III

COMPARATIVE ELECTROMOTIVE FORCES OF CONCENTRATION CELLS AT 25°C.

E.m.f. in mv.

Molality	$\gamma_{\pm}$*	E(theoretical)	E(observed)
0.01	0.7607	70.97	72.0
0.05	0.5621	20.62	20.8
0.10	0.4800	reference	-
0.20	0.4046	-20.12	-20.2
0.30	0.3556	-31.84	-31.7
0.40	0.3449	-40.70	-40.2
0.50	0.3270	-47.23	-46.9
0.926	0.279	-64.86	-64.3
1.389	0.253	-76.71	-76.3
1.852	0.234	-84.83	-84.2

*Data reported by Lortie and Demers(1)

Comparison of the theoretical and observed e.m.f. values proved the reversibility of the concentration cell reactions and the reliability of the method for evaluating the activity coefficients of sodium carbonate in solution.

RESULTS AT 15 TO 65°C.

After the reliability of concentration cell measurements was established, the e.m.f. determinations were extended from 15 to 65°C. For each concentration of sodium carbonate two or three pairs of electrodes were used to determine the e.m.f. over the whole temperature range. Since the cells tended to be unstable at the higher temperatures and readings were made after a short period of time at each temperature, variations in potentials up to 1.0 mv. were recorded in duplicate runs. It was necessary to average the data to obtain internally consistent results. The data were cross-plotted on graphs of e.m.f. versus concentration at constant temperature, e.m.f. versus temperature at constant concentration, and e.m.f. versus the logarithm of concentration at constant temperature. The most reliable data taken from the smooth curves are tabulated in Table IV. The sign of the e.m.f. is indicated in relation to the reference solution electrode at zero potential. The original data are tabulated in the Appendix. (Table XV)

TABLE IV

EQUILIBRIUM ELECTROMOTIVE FORCES
OF CONCENTRATION CELLS
AT 15 TO 65°C.

Molal Concentration	E.m.f. in mv.				
	15°	25°	37.5°	50°	65°
0.1005	reference solution		0	0	0
0.2008	-18.7	-20.2	-22.4	-24.2	-25.1
0.4009	-37.3	-40.2	-44.4	-47.0	-48.8
0.6014	-48.2	-52.1	-57.1	-59.8	-61.9
0.8470	-57.5	-62.0	-67.5	-70.2	-71.8
1.0047	-62.0	-66.8	-72.1	-75.0	-76.2
1.5355	-73.3	-78.8	-84.1	-86.8	-88.6

DENSITIES OF SODIUM CARBONATE SOLUTIONS

In the evaluation of the activity coefficients by the Debye-Hückel equation, molar concentrations rather than molal concentrations are used. Since accurate density data were necessary, laboratory determinations were made to obtain data at the desired temperatures and to check data in the literature.

Pycnometers of approximately 30 ml. capacity were calibrated with water at each temperature. Since the concentration cell bath

was covered by a layer of liquid paraffin, the pycnometers were washed with benzene and then acetone before weighings were made. About one-half of the determinations were made in duplicate. The results are listed in Table V. The data were plotted as a function of concentration at constant temperature and compared with values at 15, 25, and 50°C. listed in the International Critical Tables (16). Over the entire range the values checked within five parts in 10,000. The results are shown graphically in Figure 7, page 75.

TABLE V

DENSITIES OF SODIUM CARBONATE SOLUTIONS 15 TO 65°C.

Molal Concentration	Density in g./ml.				
	15°	25°	37.5°	50°	65°
(water)*	0.9991	0.9971	0.9932	0.9881	0.9806
0.0501	1.0050	1.0024	0.9985	0.9928	0.9857
0.1005	1.0103	1.0079	1.0036	0.9983	0.9907
0.2008	1.0205	1.0186	1.0140	1.0086	1.0008
0.4009	1.0415	1.0386	1.0340	1.0279	1.0210
0.6014	1.0620	1.0587	1.0537	1.0476	1.0404
0.8470	1.0866	1.0827	1.0769	1.0708	1.0633
1.0047	1.1006	1.0969	1.0912	1.0849	1.0768
1.5355	1.1482	1.1434	1.1372	1.1303	1.1220

*Water density reported in Lange's Handbook (17).

MEASUREMENT OF THE VAPOR PRESSURES OF SODIUM CARBONATE SOLUTIONS

The dynamic or gas saturation method of measuring vapor pressures was chosen for the salt solutions. An inert gas, such as nitrogen, is passed slowly through sufficient solution until it becomes saturated with water vapor at the existing conditions of temperature and pressure. Two general adaptations have been employed in determining the vapor pressures: (1) measuring the amount of inert gas passing through the closed system and the amount of water vapor in the gaseous phase in equilibrium with the solution, and (2) comparing the vapor pressure of the solution with that of pure water by passing the same amount of inert gas through the solution and water systems and measuring the amount of the water vapor in the gaseous phase after each system. Calculations are based on Dalton's law of partial pressures. The second method was used for this research because of the difficulties in accurately measuring the low gas flow rates required between 65 and 95°C.

APPARATUS

The apparatus included a tank of water-pumped nitrogen, presaturators, saturation cells, manometers, drying tubes, and a thermostat as shown in Figures 4 and 5. The presaturators and the saturation cells were submerged in the thermostat.

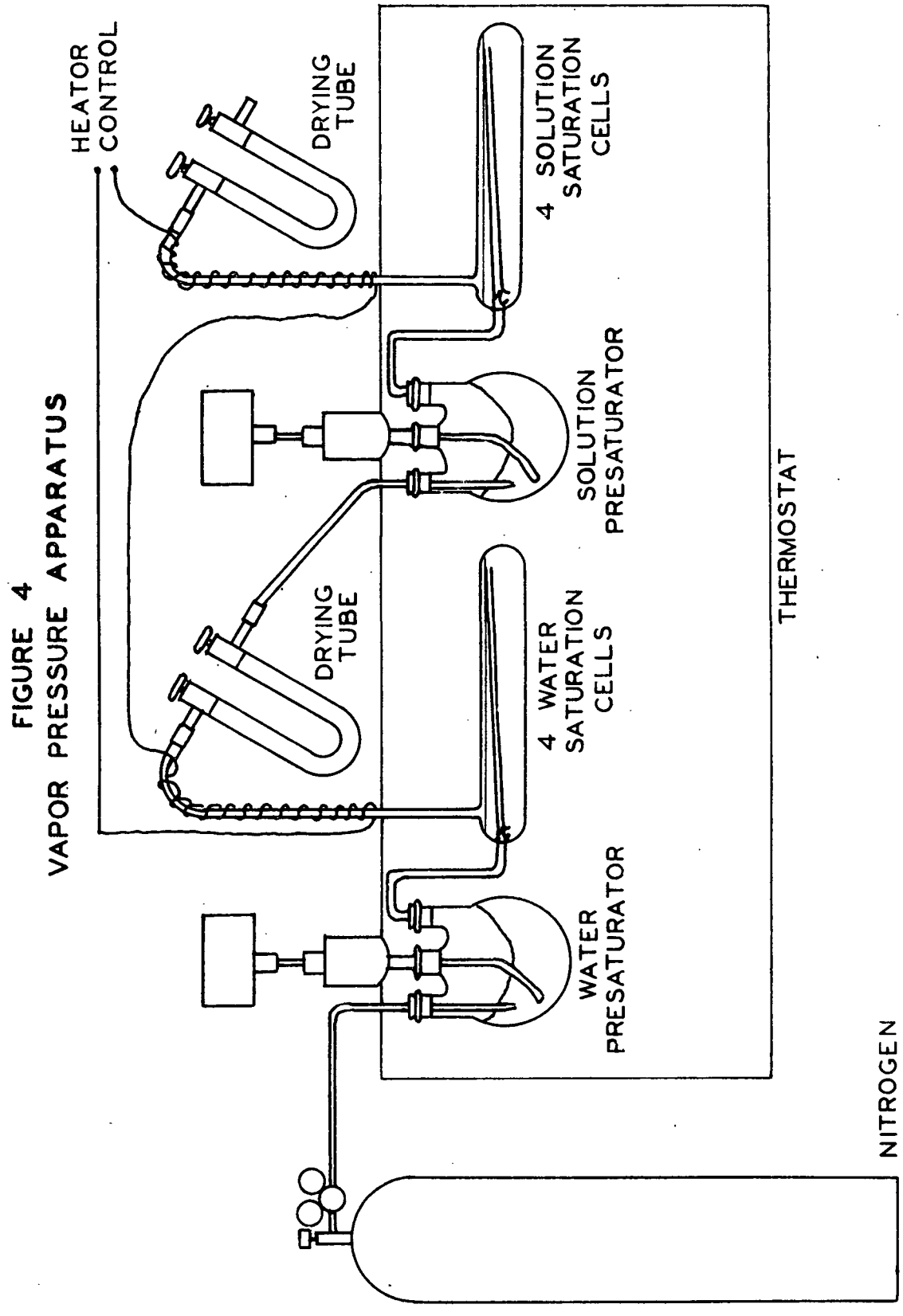


FIGURE 4
VAPOR PRESSURE APPARATUS

FIGURE 5

VAPOR PRESSURE APPARATUS

The thermostat was a galvanized metal tank which was painted on the inside and lagged on the outside with one-inch insulation board. Ethylene glycol was used in the bath because of the ease in cleaning the cells when solutions were changed and because the vapor pressure is considerably below that of water at the operating temperatures of the bath. The glycol was very satisfactory up to about 80°C., but at higher temperatures the rate of evaporation in the open tank was appreciable. Another disadvantage in the use of ethylene glycol is the toxicity of the vapors if inhaled in too great quantities.

Two shelves were fastened on top of the tank at opposite sides to support the stirrers for the bath, thermoregulator relay, and manometers for the saturation cells, and to hold the drying tubes during the experimental runs. Two brass rods were fastened through the shelves to support the submerged presaturators and their stirrers above.

A wooden rack was submerged 7 inches below the top of the tank to hold the saturation cells. A minimum number of narrow cross members was used to permit good circulation throughout the tank. Clamps to hold the cells in place were made with copper nails, wire and brass springs for easy assembly of the apparatus.

A combination of heaters was used for proper temperature control. Two 1000-watt heaters were used to provide a continuous supply of heat. By means of a three-way switch and a variable transformer sufficient

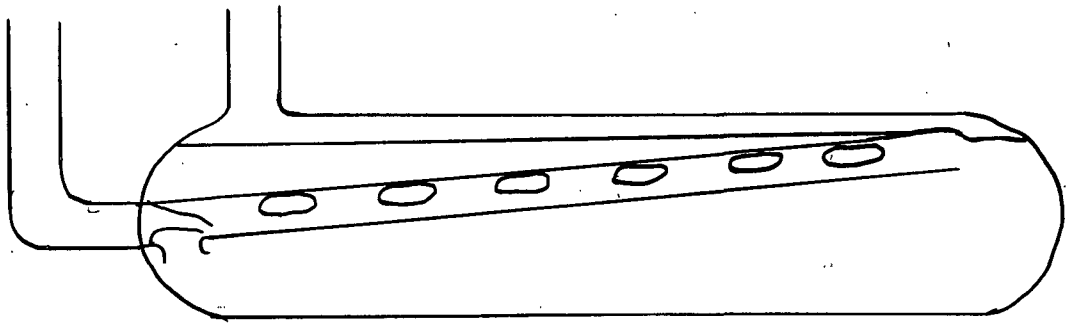
heat was added to maintain the bath at a temperature slightly below the desired control temperature. The temperature was controlled by a mercury-to-platinum thermoregulator operating a 500-watt intermittent heater. The regulators were set at 65, 80, and 95°C. with an accuracy of 0.02°C. as measured with a calibrated thermometer.

The presaturators were designed to provide maximum contact between the nitrogen and water or solution without an excessive pressure drop before the gas passed to the saturation cells. Two 1-liter, 3-neck flasks with mercury seal stirrers were used for this purpose. Stirrers were made from glass rods and shaped so that small bubbles were formed throughout the liquid, and liquid was splashed high up on the walls of the flask. Even at medium rates of stirring, very effective gas-liquid contact was maintained.

The two outer necks of the flask were connected to the rest of the system with glass tubing through rubber stoppers. The pressure fit of the stoppers in the flasks effectively sealed out the ethylene glycol in the bath. However, at the ground glass joint connecting the flasks and the mercury seals, considerable difficulty was encountered in securing a good seal. The joint was lubricated with silicone grease, and several types of plastic were applied over the outside of the joint. No type of thermoplastic or thermosetting plastic was found that would bond to the glass and not swell when exposed to ethylene glycol at

high temperature. Finally two layers of Gooch tubing were stretched completely over the mercury seal and joint section. The rubber was wired in place to exclude all ethylene glycol. The rubber slowly swells and deteriorates in the glycol, but it was sufficiently resistant for the duration of the runs.

The saturation cells are similar to those used by Pearce and Snow (18) and shown in the accompanying sketch.



The inner tube of the cell had an inside diameter of 5 mm. Gas bubbles formed at the capillary tip, moved up the inclined tube, and broke at the surface. The gas then passed over the surface of the solution before passing to the next cell. The pressure drop through each cell was about one inch of water. The capacity of the cell was 250 ml.

The glass tubing on the cells was bent and cut so that close connections with rubber tubing were possible. At first, surgical type gum rubber tubing was used for connections, but this rubber deteriorated rapidly. Tygon tubing was tested but this also became stiff and stretched in the glycol bath. Subsequently, pressure tubing was wired in place and served satisfactorily. It was necessary to replace the rubber connections after the runs for two concentrations were completed.

Manometers were connected to the last cell of both series by a glass Y-connection below the surface of the bath. A stopcock was located just above the surface to permit closing the line when the pressure was not being determined. If the manometer were left open all the time on the solution cell, the results would be affected by condensate running back and wetting the tubing above the cell. The manometers were filled with water, and the difference between the pressure in the last saturation cell of each series and atmospheric pressure was recorded for each run.

Heaters were made to cover the glass tubing leading from the last cells in the bath to the drying tubes above. These were made by wrapping the tubing with glass tape, nichrome wire, and layers of glass tape and glass wool. It was necessary to make the heated section extend to the bath level to prevent condensation. The bottom of the

heater was coated with plastic to keep the glycol from the heating elements. The temperature of the heaters was controlled by a combination of a variable resistance and an autotransformer. The top of the heated tube was bent below the horizontal to make the condensate flow into the drying tube instead of back into the heater.

The drying tubes were Schwartz absorption U-tubes with standard taper stopcocks and filled with magnesium perchlorate. The drying tubes were connected directly to the heated tubing leading from the saturation cells by a short section of rubber tubing. The exit side arm of the drying tube on the water system was connected to the inlet of the solution system presaturator by rubber tubing. The operation of the system was as follows: (1) equilibrium saturation of nitrogen in contact with pure water, (2) absorption of all water vapor from the nitrogen stream in a drying tube, (3) equilibrium saturation of the nitrogen in contact with a sodium carbonate solution, and (4) absorption of all water vapor from the nitrogen stream in a second drying tube.

EXPERIMENTAL PROCEDURES

A solution of desired concentration was prepared using weighed amounts of reagent grade sodium carbonate and twice-distilled water. Approximately 1500 ml. were sufficient for the presaturator, cells,

density samples, and analysis samples. The presaturator and cells were filled with solution and put into the thermostat where the rubber connecting tubes were wired in place. The thermostat was filled with ethylene glycol, and the temperature was adjusted to 65°C.

The water and solution systems were connected by a rubber tube, the presaturator stirrers were started, and the tube heaters were turned on. Next nitrogen was passed through the system at a high flow rate for an hour to dry the inside of the heated tubes and allow the saturation cells and connecting tubing to come to a steady state. In some of the early runs, insufficient time was allowed, and the results were erratic.

After the entire system had reached a steady operating condition, a pair of drying tubes was attached, and a run was begun. The flow of nitrogen was adjusted to about 80 $cm.^3$/minute (21°C. and 1 atmosphere pressure). During a 30 minute run at 65°C., the manometer and barometer readings were recorded periodically. There were constant minor fluctuations in the manometer readings, and the average values were determined. Four runs were made using separate pairs of drying tubes.

The thermostat temperature was increased to 80 and 95°C., and the above procedures were repeated at each temperature. At 80°C. the runs were of 20-minute duration at a nitrogen flow rate of 50 $cm.^3$/min., at 95°C. the runs were 15 minutes at a flow rate of 20 $cm.^3$/min.

Special preparation and handling of the drying tubes were necessary for obtaining reliable results. The granular anhydrous magnesium perchlorate used as a desiccant was very effective, but the tubes became plugged as the salt was wetted. To overcome this difficulty a loose rope of twisted glass wool was drawn into a drying tube from the inlet side to a point just beyond the bend in the U-tube. The loose rope filled about one-fourth the cross-sectional area of the tube. The remaining volume in the tube was filled with the desiccant. The glass wool prevented the packing and plugging of the magnesium perchlorate without reducing the effectiveness of the absorption tubes. Complete drying of the gas was assured even at the highest temperature and gas flow rates.

As mentioned previously, a drying tube was connected to the apparatus by a short section of rubber tubing which was left on the inlet side arm of the tube at all times. During a run, condensate formed in the inlet side arm of the drying tube. It was necessary to slip a glass plug into the rubber connecting tubing when the drying tube was removed from the apparatus to prevent loss due to evaporation during weighing.

In order to determine accurately the amount of water vapor absorbed by a drying tube during a run, the following procedure was adopted. In preparation for a new run, the condensate in the inlet

side arm from a previous run was removed before the tare weight of a tube was determined. With the inlet stopcock of a drying tube closed, the wet side arm was flushed with acetone to remove all the water. Most of the acetone was evaporated by applying suction with an aspirator. The drying tube with the exit stopcock open was put in an oven at 105°C. for ten minutes to remove all the surface moisture and then allowed to cool in a large desiccator. After cooling at least an hour, the tube with the exit stopcock open and the glass plug in place was weighed on a balance to 0.1 mg. to determine the tare weight. At the completion of a run, the glass plug was put into the rubber connecting tube, and the drying tube was again heated in the oven to remove condensed water or ethylene glycol vapors from the outside surfaces before cooling and determining the gross weight. Errors due to weighing were minimized using this procedure.

DETERMINATIONS OF VAPOR PRESSURE OF WATER AT OPERATING TEMPERATURES

It was necessary to establish the reliability of the apparatus in regard to complete saturation of the nitrogen passing through the cells. Therefore, the vapor pressure of the water was checked at 65 and 95°C. using Dalton's law. A Fisher and Porter variable-area flowmeter was used to determine the amount of nitrogen passed through the saturation cells during a run. A calibration chart for the flowmeters was calculated from information furnished by the manufacturer.

With the thermostat set at 65°C. the flow rate of nitrogen at 21°C. and 1 atmosphere was varied from 50 to 200 $cm.^3$/min. or three separate runs. At 95°C. the flow rate of the nitrogen was varied from 10 to 25 $cm.^3$/min. (21°C. and 1 atmosphere). Just one system consisting of a presaturator and saturation cells was used. The following measurements were made: (1) moles of nitrogen passing through the cells, (2) moles of water absorbed in the drying tube, (3) barometric pressure, and (4) the differential pressure between atmospheric and that in the last cell. The vapor pressure was calculated by Dalton's law. The vapor pressure of water at 65 and 95°C. checked within 0.5% of the values listed in the handbooks, and the reliability of the apparatus was proved.

BAROMETER CORRECTION

In the method chosen for determining the vapor pressure of salt solutions, the accuracy of the barometric pressure was of great importance. The accuracy of the setting of the adjustable barometer scale was checked by comparison with a 24-inch steel height gage calibrated in 0.0001-inch divisions. A cathetometer with a brass scale was used to compare measurements. At 73°F. an average error of 0.75 mm. in scale setting on the barometer was determined. When the temperature correction for calibration of the scale at 0°C. was applied, the total correction for the barometer scale reading was minus 1.0 mm.

In addition to the scale correction, a temperature correction for the linear expansion of brass and the cubical expansion of mercury was applied to convert the readings at room temperature to 0°C. In most cases this correction was between 2 and 3 mm. of mercury. The other corrections for latitude and gravity at sea level were negligible.

RESULTS

The vapor pressures of solutions of 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 1.5, 2.0, and 2.5 m were determined in the first series of experiments at 65, 80, and 95°C. Erratic results were obtained from a few of the early runs due to experimental technique and additional runs were made at 0.15, 0.5, 0.7, and 1.15 m to obtain more reliable results. All the experimentally determined vapor pressures were graphed as a function of concentration at constant temperature, and a smooth curve was drawn through the points. The best values were read from the smooth curve and are listed in Table VI. The estimated maximum errors in the results were 0.2 to 0.5%. Complete compilations of the experimental results are included in the Appendix. (Table XVI)

The method chosen for determining the vapor pressure was very sensitive to small errors in weighing the drying tubes for runs at 65°C. An error of one milligram in the total tube weight of about 140 grams caused vapor pressure errors up to 0.3 mm. of mercury.

TABLE VI

VAPOR PRESSURES OF SODIUM CARBONATE SOLUTIONS FROM 65 TO 95°C.

Molality	Vapor Pressure in mm. Hg		
	65°	80°	95°
(water)	187.6	355.3	634.3
0.1009	186.8	353.5	631.4
0.1507	186.4	352.6	629.9
0.1999	185.9	351.9	628.7
0.4013	184.4	349.2	623.8
0.5017	183.6	347.9	-
0.5994	182.9	346.6	619.0
0.6934	182.2	-	-
0.8046	181.5	344.3	614.3
1.001	180.2	342.1	610.2
1.146	179.3	340.5	607.4
1.444	177.3	337.4	601.8
1.519	176.7	336.7	600.4
2.011	173.7	330.8	589.8
2.520	169.8	324.1	578.2

At the higher temperatures, the accuracy of the cell pressure measurements became the dominant factor in the calculation of the vapor pressure.

During a normal series of runs at each concentration, approximately 15 to 20 grams of water were removed from the sodium carbonate solution. To determine if the evaporation changed the concentration of the solution in the saturation cells, nitrogen was bubbled through the 0.2 m solution at 95°C. for an extended period until about 50 grams of water were removed. The solutions from the cells and presaturator were subsequently analyzed. The cell solutions were essentially equal to the original concentration, whereas a significant change in concentration was measured only in the presaturator.

Even though Pyrex glass was used in the presaturator and cells, the glass was attacked by the sodium carbonate solutions above 0.4 to 0.6 m. Flakes of insoluble material were evident when the glassware was taken from the thermostat. The glass surface was etched and a white film could be loosened only by boiling water or hot dilute acid. There was no measurable change in the concentration of the carbonate solutions, and the effect on the vapor pressure of the solutions appeared to be negligible.

The results at 95°C., typical of the results at the other temperatures, are shown graphically in Figure 6.

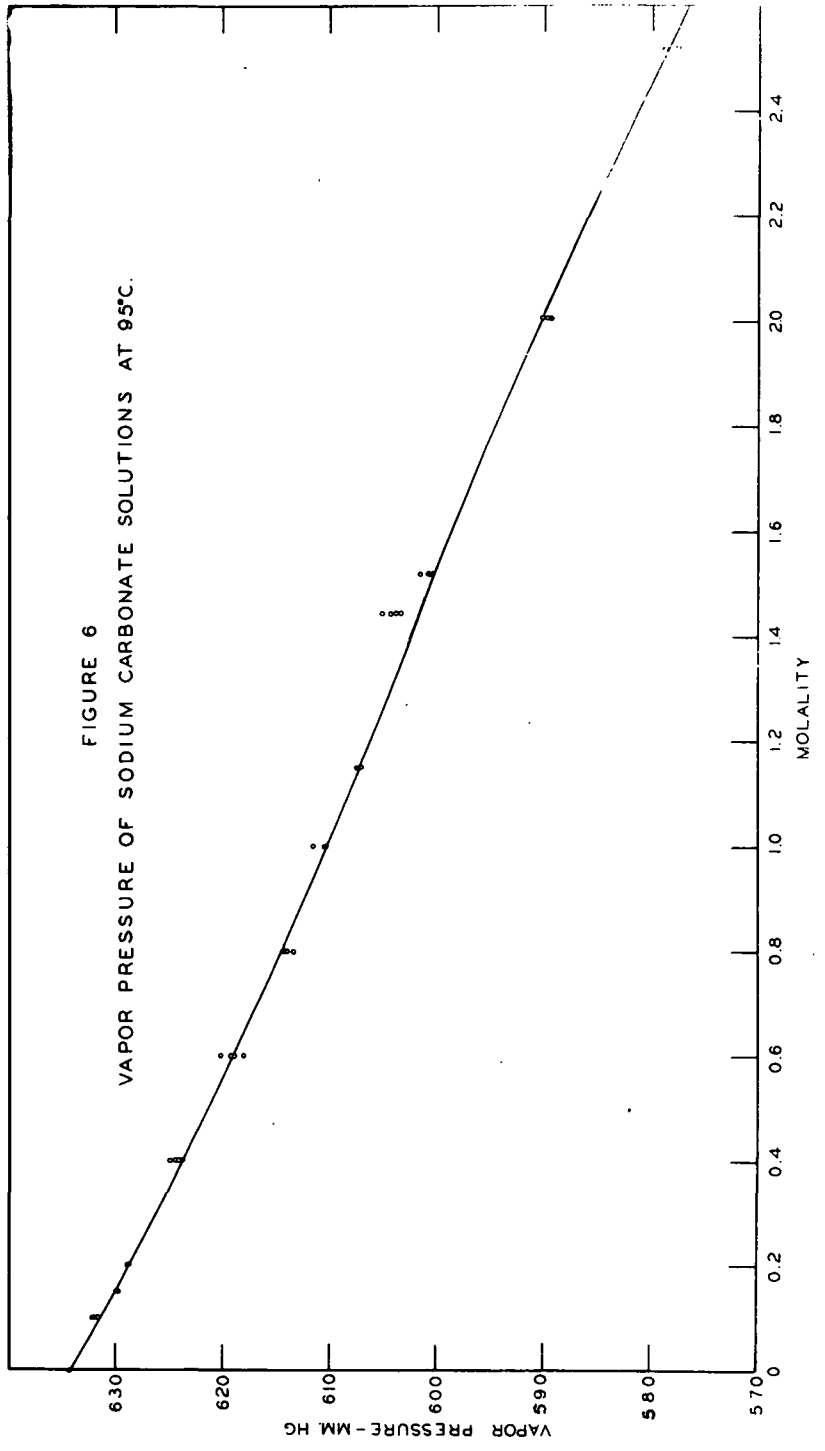


FIGURE 6

VAPOR PRESSURE OF SODIUM CARBONATE SOLUTIONS AT 95°C.

DENSITIES OF SOLUTIONS FROM 65 TO 95°C.

The densities of the sodium carbonate solutions were obtained using pycnometers which were calibrated at each temperature with water to determine the true volumes. Since ethylene glycol was used in the thermostat, the pycnometers were removed from the bath after they reached equilibrium temperature and rinsed with both water and acetone. The dry pycnometers were weighed to 1 mg. on an analytical balance.

The results are given in Table VII. The results were plotted as a function of concentration (Figure 7) and checked with the values listed in the International Critical Tables (16) at 80°C. within 5 parts in 10,000.

TABLE VII

DENSITIES OF SODIUM CARBONATE
SOLUTIONS 65 TO 95°C.

Molal Concentration	Density in g./ml.		
	65°	80°	95°
water	0.9806	0.9718	0.9619
0.1009	0.9909	0.9814	0.9718
0.1507	0.9953	0.9872	-
0.1999	1.0012	0.9922	0.9831
0.4013	1.0211	-	1.0022
0.5017	1.0302	1.0214	-
0.5994	1.0402	1.0310	1.0215
0.8046	1.0589	1.0499	1.0398
1.001	1.0768	1.0669	1.0572
1.146	1.0891	1.0799	-
1.444	1.1151	1.1058	1.0960
2.011	1.1613	1.1518	1.1414
2.520	1.1992	1.1896	1.1791

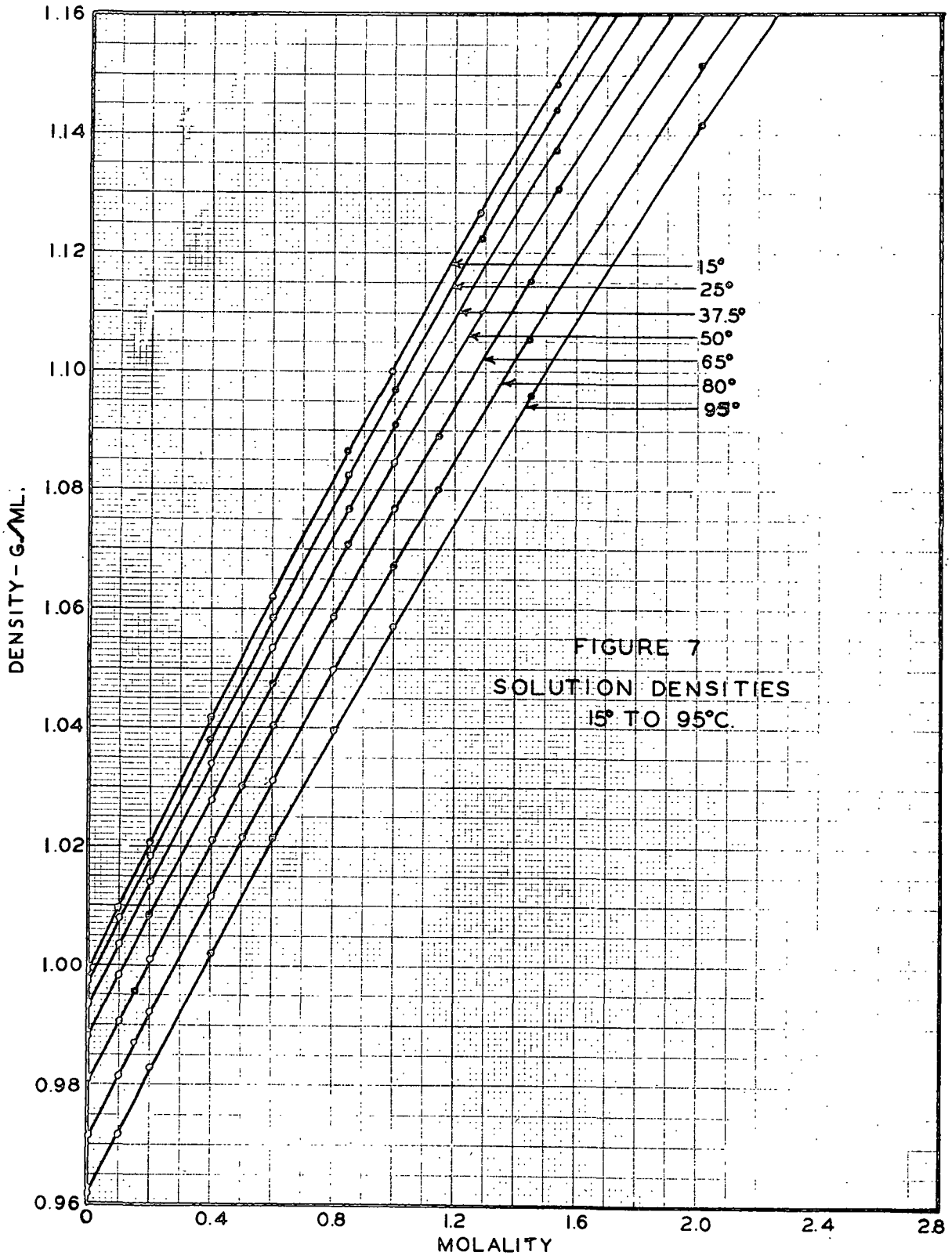


FIGURE 7
SOLUTION DENSITIES
15° TO 95°C.

THERMODYNAMIC DATA DERIVED FROM EXPERIMENTAL RESULTS

ACTIVITY COEFFICIENTS AT 25°C.

From the e.m.f. values listed in Table II, the ratio $\gamma_{\pm 2}/\gamma_{\pm r}$ may be calculated using Equation (46) and the appropriate values of E, m_2 and m_r.

$$\log \gamma_{\pm 2}/\gamma_{\pm r} = EN\mathcal{F}/(2.3)RT\ \nu - \log m_{\pm 2}/m_{\pm r} \qquad (91)$$

In order to calculate the absolute values of all the activity coefficients, $\gamma_{\pm r}$ must be evaluated by extrapolating the experimental results to infinite dilution using the Debye-Hückel equation and the procedure outlined in the theory section of this thesis. For the calculations the following constants were used:

$R = 8.314$ joules/deg.-mole

$T = 298.17°K$

$\mathcal{F} = 96,501$ coulombs/g-equivalent

$$(2.303)\nu RT/N\mathcal{F} = (2.303)(3)(8.314)(298.17)/(2)(96,501)$$
$$= 0.088725 \text{ volts} = 88.725 \text{ mv.}$$
$$S_f = 0.7164 \quad (20)$$

Sample calculations are included in the Appendix. Using Equations (59) through (65),

$A = 0.878$

$B = 0.001$

The activity coefficient of the reference solution was calculated using Equation (66)

$$\log \gamma_{\pm} = -0.7164 \sqrt{\Gamma}/1+0.878 \sqrt{\Gamma} + 0.001c-\log(1+0.018m) \quad (92)$$

Finally $\gamma_{\pm 2}$ for all solutions other than the reference solution was calculated from Equation (91). Corrections for the hydrolysis were calculated and found to be negligible at 0.1 m and higher concentrations.

In Table VIII are listed the activity coefficient data derived from the equilibrium e.m.f. of concentration cells without liquid junction at 25°C. The value of the activity coefficient reference solution is shown in parentheses to indicate that it was calculated by the Debye-Hückel equation. In order to show the accuracy with which the Debye-Hückel equation fits the experimental data and the applicable concentration range, the activity coefficients $\gamma_{\pm}$(Debye-Hückel) calculated by this equation are also listed. To indicate the variance in the data from the simple Debye-Hückel Equation (47), the results are plotted as a function of $\sqrt{\Gamma}$ in Figure 8. The limiting slopes of other valence types are also shown.

For the sake of comparison, the original data of Lortie and Demers (1) and Saegusa (2) are presented in Table IX. The data from all three investigations are shown graphically in Figure 9.

TABLE VIII

ACTIVITY COEFFICIENTS AT 25°C.

Molality	$\gamma_{\pm}$	$\gamma_{\pm}$(D.H.)*
0.0102	0.724	0.719
0.0475	0.555	0.551
0.1007	(0.465)	0.465
0.2005	0.393	0.394
0.4039	0.333	0.331
0.6130	0.299	0.299
0.8060	0.281	0.279
0.9991	0.264	0.264
1.514	0.238	0.238
2.009	0.220	0.220
2.510	0.202	-

*Calculated by the Debye-Hückel equation

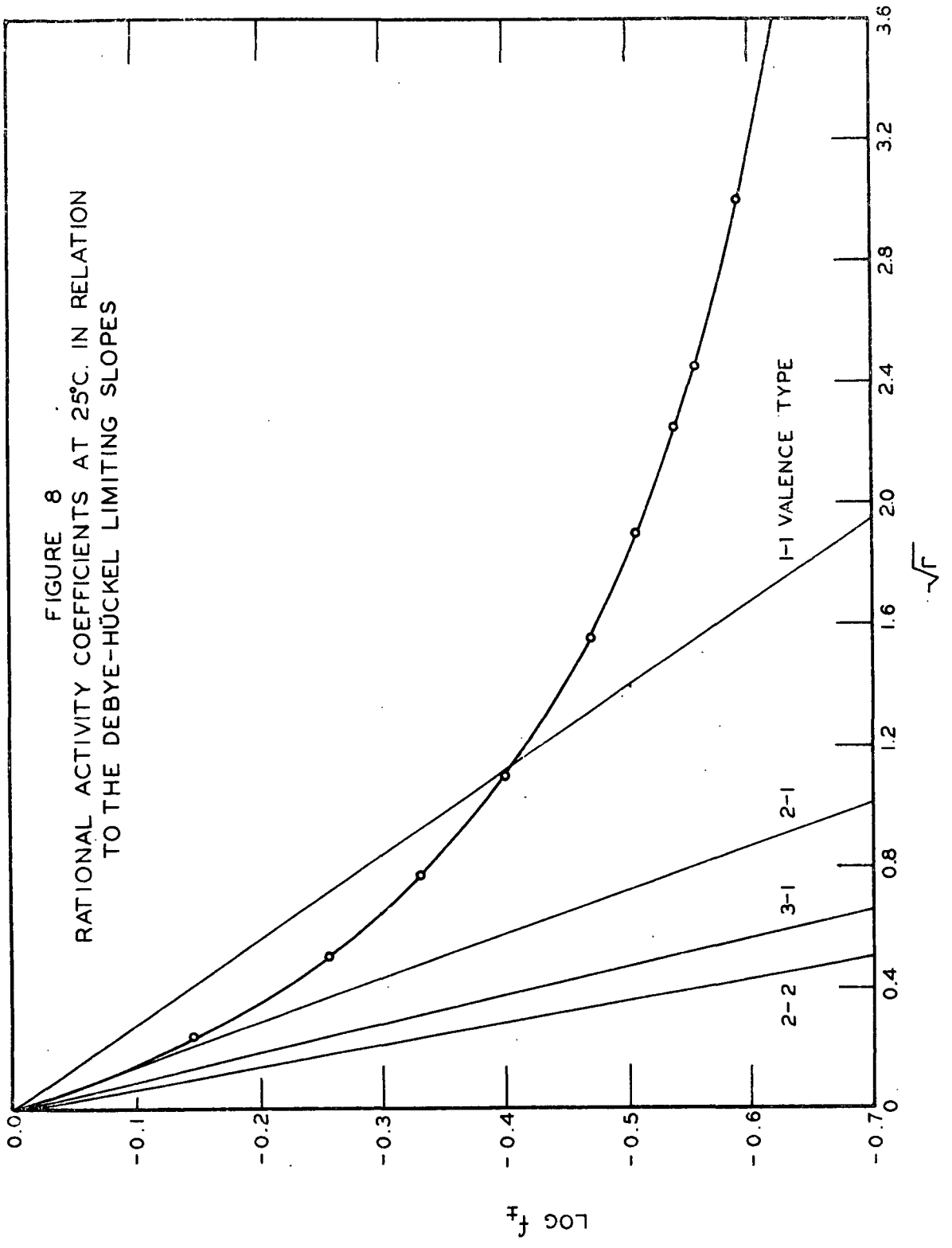


FIGURE 8
RATIONAL ACTIVITY COEFFICIENTS AT 25°C. IN RELATION TO THE DEBYE-HÜCKEL LIMITING SLOPES
1-1 VALENCE TYPE
2-1
3-1
2-2
LOG $f_\pm$
$\sqrt{\Gamma}$
0.0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
0
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
3.6

TABLE IX

ACTIVITY COEFFICIENTS AT 25°C.
PREVIOUSLY REPORTED

Lortie and Demer		Saegusa	
Molality	$\gamma_{\pm}$	Molality	$\gamma_{\pm}$
0.005	0.824	0.0011	0.899
0.01	0.761	0.0022	0.848
0.02	0.681	0.0052	0.769
0.03	0.629	0.0102	0.700
0.05	0.562	0.0206	0.633
0.1	0.480	0.0574	0.497
0.2	0.405	0.1069	0.420
0.3	0.366	0.5055	0.252
0.4	0.345	0.9777	0.220
0.463*	0.334	2.7466	0.158
0.5	0.327		
0.926*	0.279		
1.389*	0.253		
1.852*	0.234		

*Derived from vapor pressure data

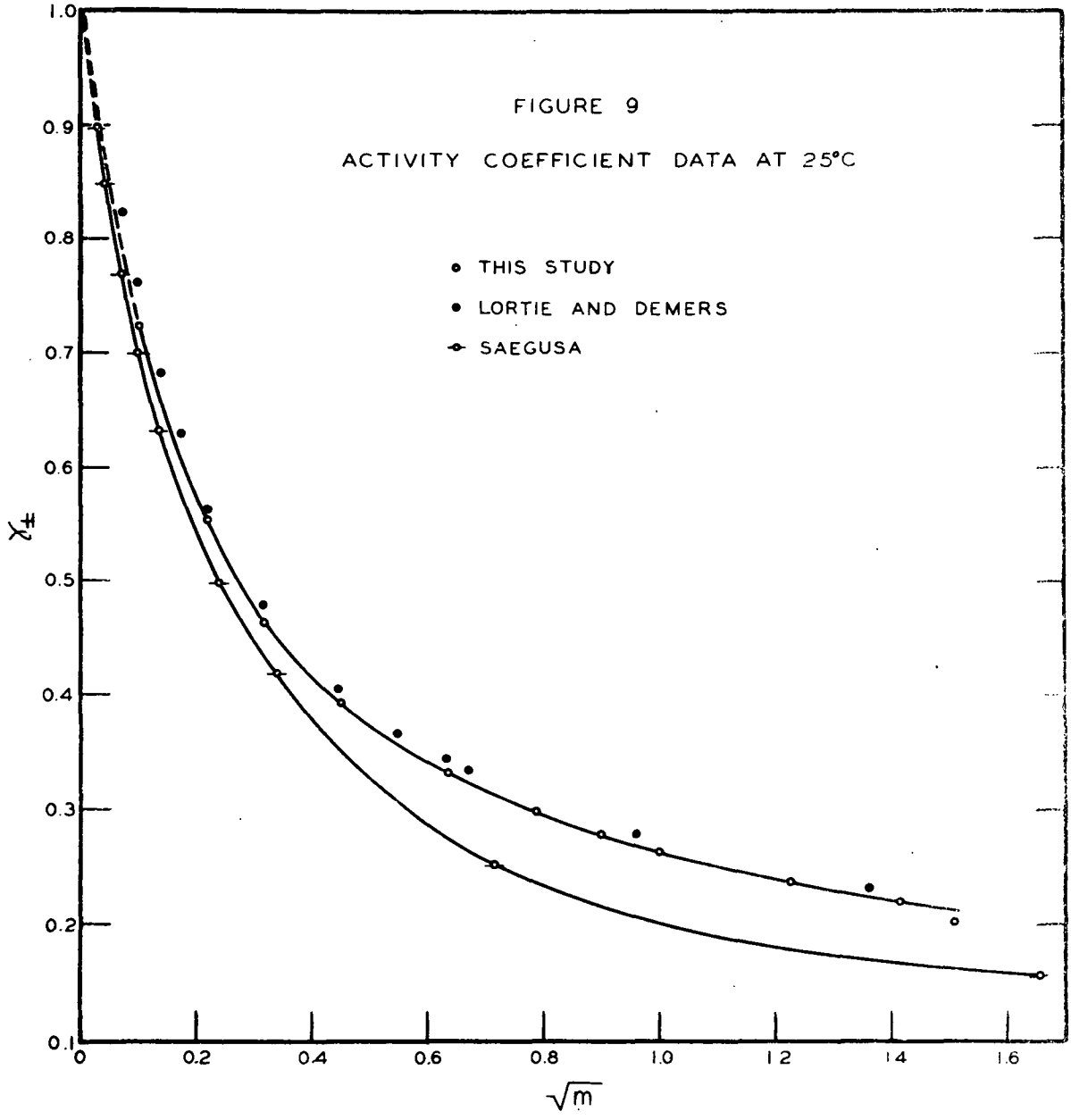


FIGURE 9
ACTIVITY COEFFICIENT DATA AT 25°C
THIS STUDY
LORTIE AND DEMERS
SAEGUSA
γ±
√m
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6

ACTIVITY COEFFICIENTS AT 15 TO 65°C. FROM CONCENTRATION CELL DATA

From the equilibrium e.m.f. of concentration cells at 15 to 65°C. in Table IV, activity coefficients were calculated using the procedure outlined in the previous section. The following values of the constant in Equations (58) and (59) were calculated:

Temperature, °C.	$3/2\ RT/\mathcal{F}\ (1000)(2.303)$, mv.
15	85.749
25	88.725
37.5	92.445
50	96.166
65	100.63

For the Debye-Hückel equation, the limiting slope, S_f, (20) and the values for the constants A and B calculated from experimental data are as follows:

Temperature, °C.	S_f	A	B
15	0.7018	0.729	0.014
25	0.7164	0.878	0.001
37.5	0.7346	1.235	-0.045
50	0.7554	1.504	-0.084
65	0.7844	1.700	-0.127

The results of the calculations are summarized in Table X and shown graphically in Figures 10, 11, and 12. The values of the activity coefficient for the 0.1 m reference solution were calculated from the Debye-Hückel equation and shown in parentheses, whereas the activity coefficients at all other concentrations were calculated by the

TABLE X

ACTIVITY COEFFICIENTS AT 15 TO 65°C.

Molality		15°	25°	37.5°	50°	65°
0.1005	$\gamma_{\pm}$	(0.448)	(0.465)	(0.504)	(0.524)	(0.529)
	$\gamma_{\pm}$(D.H.)	0.448	0.465	0.504	0.524	0.529
0.2008	$\gamma_{\pm}$	0.371	0.393	0.441	0.466	0.471
	$\gamma_{\pm}$(D.H.)	0.372	0.394	0.441	0.464	0.469
0.4009	$\gamma_{\pm}$	0.306	0.331	0.382	0.405	0.405
	$\gamma_{\pm}$(D.H.)	0.306	0.332	0.382	0.404	0.405
0.6012	$\gamma_{\pm}$	0.273	0.300	0.349	0.367	0.365
	$\gamma_{\pm}$(D.H.)	0.273	0.300	0.349	0.367	0.363
0.8470	$\gamma_{\pm}$	0.249	0.276	0.321	0.334	0.325
	$\gamma_{\pm}$(D.H.)	0.248	0.275	0.321	0.334	0.324
1.0047	$\gamma_{\pm}$	0.237	0.263	0.303	0.316	0.303
	$\gamma_{\pm}$(D.H.)	0.237	0.264	0.303	0.316	0.301
1.5355	$\gamma_{\pm}$	0.210	0.230	0.268	0.274	0.263
	$\gamma_{\pm}$(D.H.)	0.210	0.230	0.267	0.267	0.253

fundamental equation for concentration cells (91). It is obvious that errors in the extrapolation of the experimental data and the evaluation of the reference solution activity coefficient effect all the derived data. Activity coefficients, $\gamma_{\pm}$(D.H.), for each solution were calculated by the Debye-Hückel equation and listed in Table X for comparison.

In the calculation of the data, the errors due to hydrolysis were determined using Equations (69) to (78) and the procedure outlined on page 32. By neglecting hydrolysis, the maximum error in $m_{\pm 2}/m_{\pm r}$ was 0.7% at 50°C. and m_2 = 1.5 m. At lower temperatures and values of m_2,

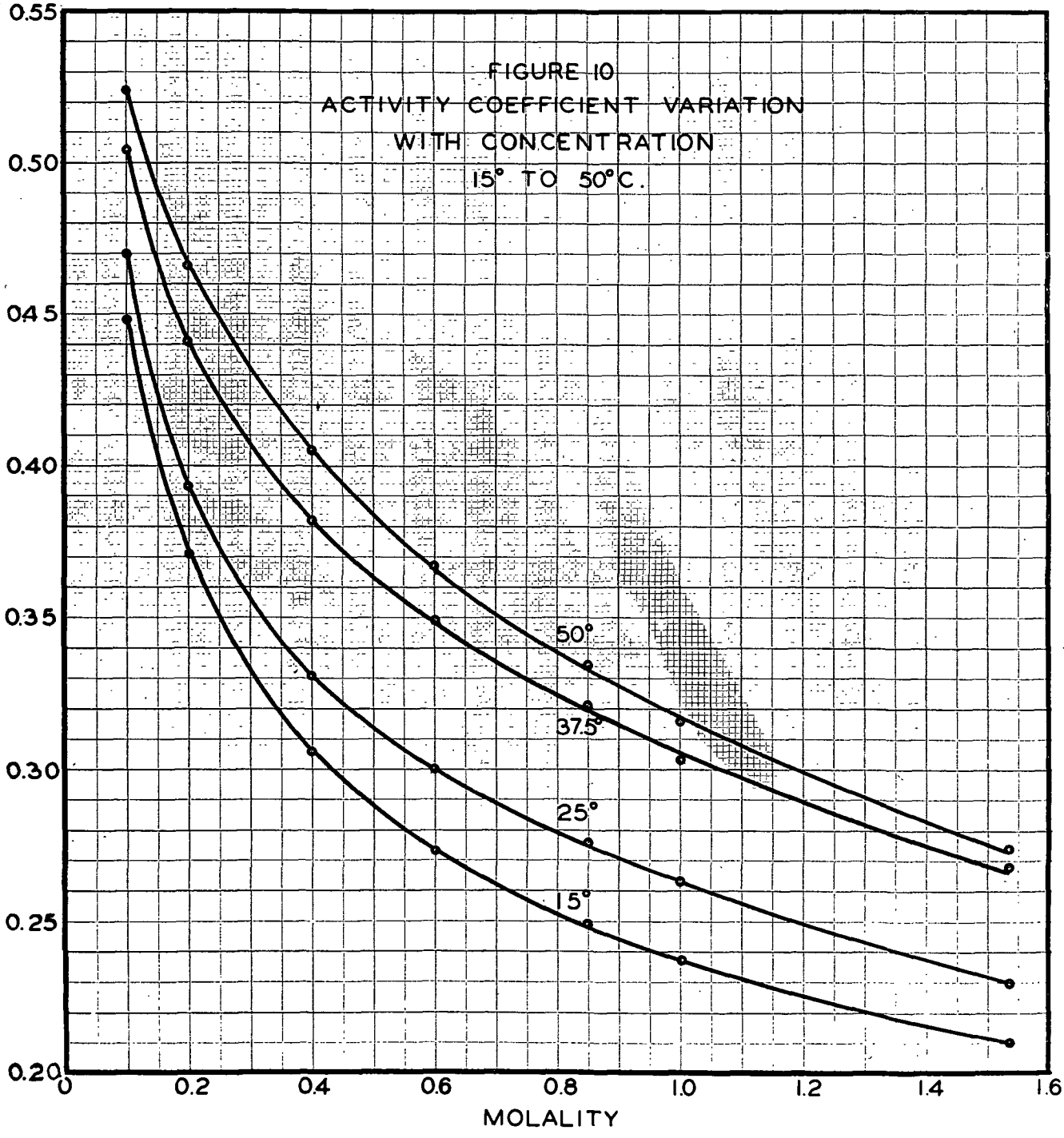


FIGURE 10
ACTIVITY COEFFICIENT VARIATION
WITH CONCENTRATION
15° TO 50°C.
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
γ±
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
MOLALITY
50°
37.5°
25°
15°

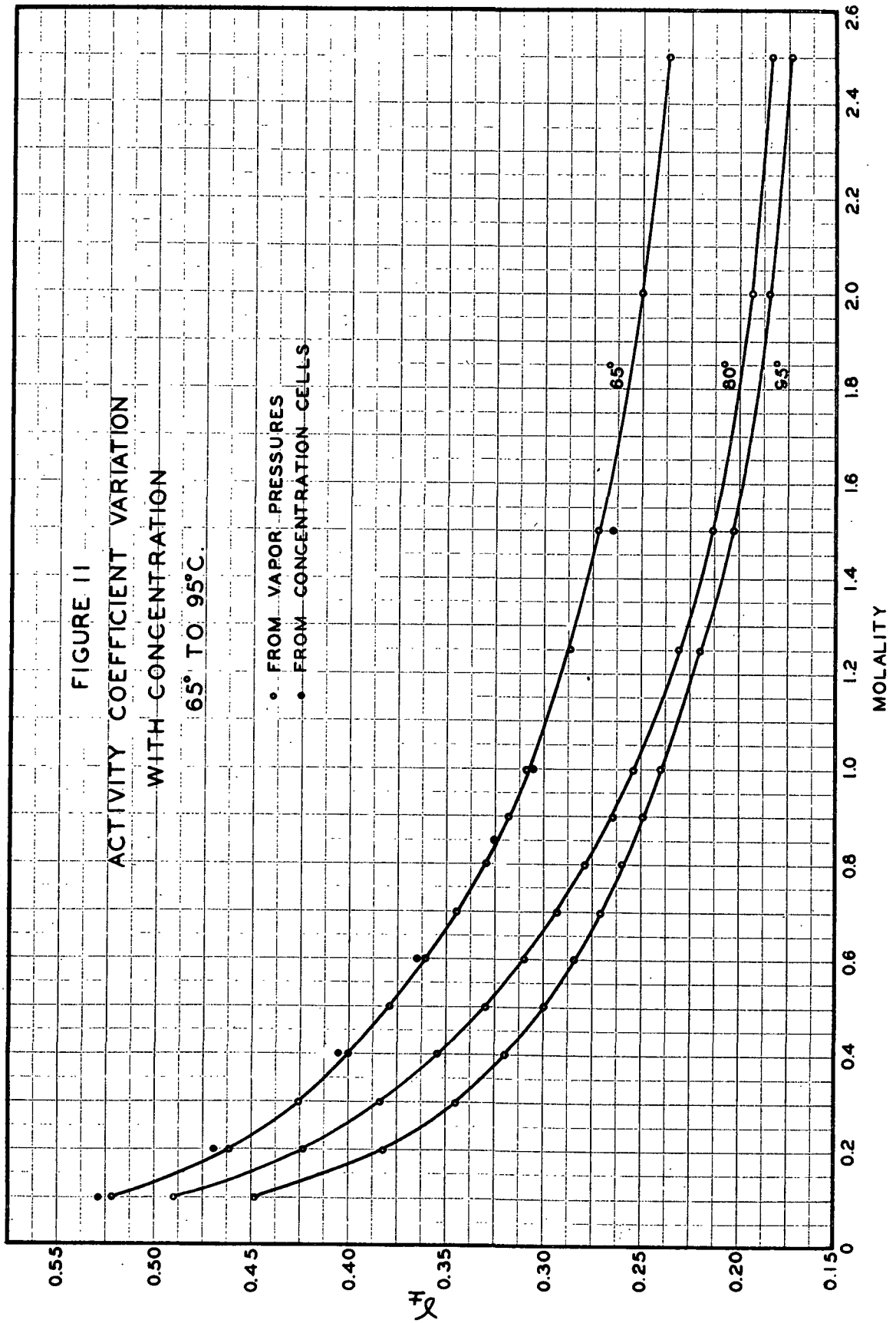


FIGURE 11
ACTIVITY COEFFICIENT VARIATION
WITH CONCENTRATION
65° TO 95°C.
• FROM VAPOR PRESSURES
• FROM CONCENTRATION CELLS
65°
80°
95°
$\gamma_\pm$
MOLALITY
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6

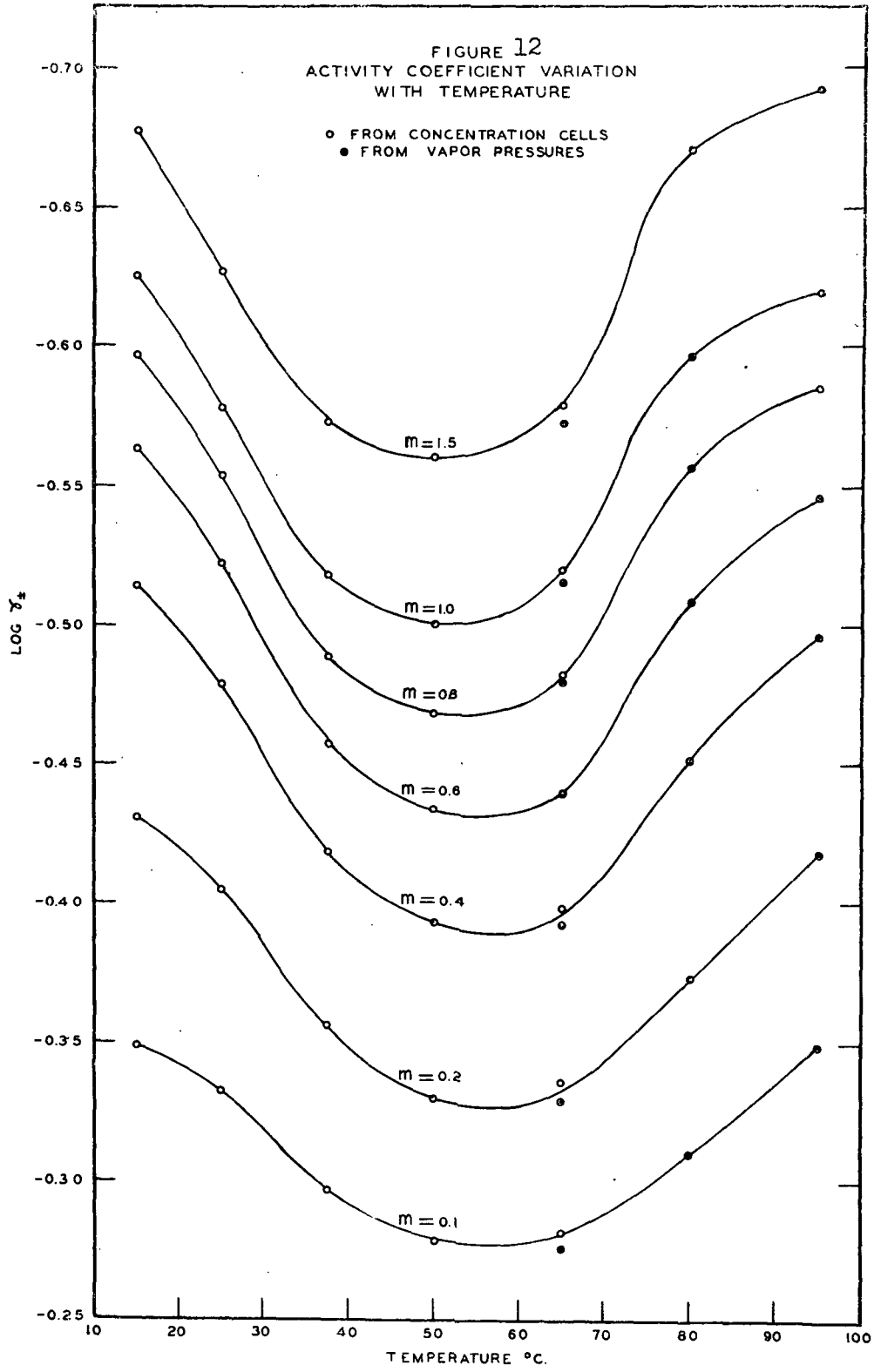


FIGURE 12
ACTIVITY COEFFICIENT VARIATION
WITH TEMPERATURE
o FROM CONCENTRATION CELLS
● FROM VAPOR PRESSURES
m=1.5
m=1.0
m=0.8
m=0.6
m=0.4
m=0.2
m=0.1
LOG γ±
-0.70
-0.65
-0.60
-0.55
-0.50
-0.45
-0.40
-0.35
-0.30
-0.25
10
20
30
40
50
60
70
80
90
100
TEMPERATURE °C.

the errors were considerably smaller. Therefore, the corrections for hydrolysis over the experimental concentration range were not necessary.

ACTIVITY COEFFICIENTS FROM VAPOR PRESSURE MEASUREMENTS AT 65 TO 95°C.

The e.m.f. values of concentration cells yield a direct measure of the logarithmic ratios of activity coefficients. However, vapor pressure measurements yield the activity of the solvent (water), and integration of the Gibbs-Duhem equation is necessary to determine the corresponding logarithmic ratios of the activity coefficients.

$$\log \gamma_{\pm 2}/\gamma_{\pm r} = -\int_{a_1 \text{ at } m_1}^{a_1 \text{ at } m_2} 18.052/m \; d \log a_1 - \log m_2/m_1 \qquad (83)$$

$$\ln \gamma_{\pm 2}/\gamma_{\pm r} = (\varphi_2 - \varphi_1) - 2\int_{m_1}^{m_2} (1-\varphi)/m^{1/2} \; dm^{1/2} \qquad (33)$$

Integration of Equations (83) and (33) yields the same results, but the magnitude of the errors in evaluation is reduced using Equation (33). Both equations were used to calculate the data at 65°C., and only Equation (83) was used at 80 and 95°C.

For calculation purposes a reference solution of 0.4000 m was chosen. A lower concentration was not used to avoid accumulative errors due to hydrolysis and more difficult graphical integrations

at concentrations below 0.4 m. It was estimated that the vapor pressure data were accurate to 0.2 to 0.5%. However, in the graphical integration of the term containing the activity of the water ($\log a_1$) it was necessary to estimate the vapor pressure to 0.01 mm. Hg at 65°C. and 0.5 mm. Hg at 80 and 95°C. from the smooth vapor pressure curves. The sensitivity of the activity term may be illustrated by the following example:

$$P_1 = 186.78 \quad ; \quad \log a_1 = -0.00202$$

$$P = 186.79 \quad ; \quad \log a_1 = -0.00199$$

An intermediate graph of m versus $\log a_1$ was made at each temperature to average the data. The results of the integration are listed in Table XI.

The process of extrapolating $\log \gamma_{\pm 2}/\gamma_{\pm r}$ by the Debye-Hückel equation and the evaluation of constants A and B was carried out as described in the theory section using Equations (84) through (89). The values of the limiting slope, S_f, used in the calculations and the determined values of A and B are as follows:

Temperature, °C.	S_f	A	B
65°	0.7844	1.615	-0.109
80°	0.8166	1.480	-0.153
95°	0.8524	1.202	-0.072

TABLE XI

EVALUATION OF EQUATION (83) USING GRAPHICAL INTEGRATION

	65°C.		80°C.		95°C.	
Molal Conc.	P (mm.Hg)	$\log \frac{\gamma_{\pm 2}}{\gamma_{\pm 0.4}}$	P (mm.Hg)	$\log \frac{\gamma_{\pm 2}}{\gamma_{\pm 0.4}}$	P (mm.Hg)	$\log \frac{\gamma_{\pm 2}}{\gamma_{\pm 0.4}}$
0.0000	187.65	-	353.30	-	634.30	-
0.1000	186.78	+0.1153	353.45	+0.1406	631.40	+0.1471
0.2000	185.95	+0.0623	351.95	+0.0770	628.75	+0.0778
0.3000	185.14	+0.0278	350.50	+0.0357	626.20	+0.0345
0.4000	184.38	reference	349.15	reference	623.80	reference
0.5000	183.62	-0.0238	347.85	-0.0303	621.45	-0.0272
0.6000	182.90	-0.0452	346.65	-0.0574	619.00	-0.0502
0.7000	182.21	-0.0651	345.45	-0.0829	616.70	-0.0708
0.8000	181.53	-0.0828	344.35	-0.1056	614.40	-0.0896
0.9000	180.86	-0.0990	343.20	-0.1262	612.25	-0.1075
1.0000	180.21	-0.1138	342.10	-0.1446	610.20	-0.1238
1.2500	178.56	-0.1452	339.50	-0.1856	605.50	-0.1612
1.5000	176.86	-0.1682	336.90	-0.2198	600.75	-0.1963
2.0000	173.72	-0.2038	330.95	-0.2624	390.10	-0.2384
2.5000	169.98	-0.2274	324.40	-0.2871	578.70	-0.2654

From the values of A and B the activity coefficients of the 0.4 m reference solution at 65, 80, and 95°C. were calculated by the Debye-Hückel equation.

$$\log \gamma_{\pm} = -S_f\sqrt{\Gamma}/1+A\sqrt{\Gamma} + Bc - \log (1+0.054\ m) \qquad (93)$$

The activity coefficients of the other solutions were calculated directly from the logarithmic ratios in Table XI. The activity coefficients, $\gamma_{\pm}$ (D.H.), from 0.1 m to 1.0 m were also calculated from the Debye-Hückel equation. The activity coefficients derived from the vapor pressures of sodium carbonate solutions are summarized in Table XII. Sample calculations are included in the Appendix. The results are shown graphically in Figures 11 and 12.

RELATIVE PARTIAL MOLAL ENTHALPIES

The relative partial molal enthalpy of a solute ($\bar{L}_2$) is defined by Equation (37).

$$\bar{L}_2 = -\nu RT^2\, \partial \ln \gamma_{\pm}/\partial T \qquad (37)$$

The logarithms of the activity coefficient data from Tables X and XII were graphed as a function of temperature at constant concentration as shown in Figure 12. The slopes of the curves were measured at 25, 37.5, 50, 65, and 80°C. using the front face mirror technique, and $\bar{L}_2$ was calculated from Equation (37). The results are shown in Table XIII.

TABLE XII

ACTIVITY COEFFICIENTS FROM
VAPOR PRESSURE MEASUREMENTS

Molal Conc.	65°C.		80°C.		95°C.	
	$\gamma_{\pm}$	$\gamma_{\pm}$(D.H.)	$\gamma_{\pm}$	$\gamma_{\pm}$(D.H.)	$\gamma_{\pm}$	$\gamma_{\pm}$(D.H.)
0.1000	0.522	0.522	0.489	0.490	0.448	0.449
0.2000	0.462	0.462	0.423	0.423	0.382	0.382
0.3000	0.426	0.426	0.384	0.383	0.345	0.344
0.4000	(0.400)	0.400	(0.354)	0.354	(0.319)	0.319
0.5000	0.379	0.379	0.330	0.330	0.300	0.300
0.6000	0.361	0.361	0.310	0.310	0.284	0.284
0.7000	0.345	0.345	0.293	0.293	0.271	0.271
0.8000	0.330	0.330	0.278	0.278	0.260	0.260
0.9000	0.318	0.317	0.264	0.263	0.249	0.249
1.0000	0.308	0.305	0.254	0.251	0.240	0.240
1.2500	0.286	-	0.231	-	0.220	-
1.5000	0.272	-	0.213	-	0.203	-
2.0000	0.250	-	0.193	-	0.184	-
2.5000	0.237	-	0.183	-	0.173	-

TABLE XIII

RELATIVE PARTIAL MOLAL ENTHALPIES
OF SODIUM CARBONATE IN SOLUTION

$\bar{L}_2$ in cal./mole

Molality	18°C.*	25°C.	37.5°C.	50°C.	65°C.	80°C.
0.10	-150	-291	-335	-122	+172	+386
0.20	-520	-413	-425	-160	+223	+504
0.40	-1120	-501	-438	-166	+332	+662
0.60	-1730	-622	-405	-118	+414	+705
0.80	-2110	-624	-436	-66	+520	+639
1.00	-2460	-631	-447	-31	+675	+460
1.50	-2660	-642	-332	-14	+616	+351

*Calculated from data of Bichowsky and Rossini (11)

The only means of comparing the results of this study with previous thermochemical measurements is to calculate $\bar{L}_2$ from the enthalpies of solutions at 18°C. reported by Bichowsky and Rossini (8) and Equation (40).

$$\bar{L}_2 = -\Delta H_D - 1/2\sqrt{m}\,\partial \Delta H_D/\partial\sqrt{m} \qquad (40)$$

The enthalpies were based on a few thermochemical measurements above 0.28 m; below 0.28 m all the values were estimated. Since the heat of dilution ΔH_D depends on the value of the estimated enthalpy at infinite dilution

$$H_D \equiv H(m) - H^\circ(m=0),$$

any errors in H° due to experimental technique or heat effects caused by hydrolysis are magnified using Equation (40). The results of the calculations using Equation (40) are also shown in Table XIII.

DISCUSSION OF THERMODYNAMIC DATA

In the previous section, the methods of calculating the thermodynamic data were summarized, and the results were presented. It is very important to realize that the experimentally determined electromotive forces and solution vapor pressures yield valid measures of the free energy changes of dilution. The only uncertainty in the data arises in the calculation of the absolute values of the activity coefficients and relative partial molal enthalpies. It is necessary to consider further the reliability of these results and to discuss the utility of the thermodynamic data.

RELIABILITY OF ACTIVITY COEFFICIENT DATA AT 25°C.

The first consideration in the reliability of the activity coefficient data is the comparison of the results from this investigation with those previously reported in the literature. The data are shown graphically in Figure 9. The only discrepancies in the data appear to be due to errors in determining the absolute values of the activity coefficients and not to any errors in the measure of the free energy changes over the experimental concentration range. As mentioned previously, Lortie and Demers (1) estimated that their results were 2.6 to 3.1% high. If these corrections are applied, the results from the concentration cells and the combined results from freezing point

depression measurements and vapor pressure are in excellent agreement. The results of Saegusa (2) are significantly low over the entire concentration range. The inaccuracies in his method of extrapolation to infinite dilution account for the erroneous value of E° and, subsequently, for the absolute values of all the activity coefficients. Considering the fact that three different methods of measurement and extrapolation were employed, agreement of the results is satisfactory. Use of the Debye-Hückel equation for purposes of extrapolation appears to reduce the uncertainties in the derived results.

Another means of checking the reliability of the absolute values of the activity coefficients is the calculation of the pH of a dilute solution and comparison with the measured pH at the same concentration and temperature. From Equations (70) and (72)

$$\gamma_{Na^+} \cong \gamma_{OH^-} \cong \gamma_{\pm}^{1/2} \; Na_2CO_3 \tag{94}$$

From Equation (73)

$$a_{OH^-} = mx\,\gamma_{OH^-} \cong mx\,\gamma_{\pm}^{1/2} \tag{95}$$

Since the activity of water is approximately equal to unity in dilute solution, the activity of the hydrogen ion is given by the equation

$$a_{H^+} = K_W/a_{OH^-} \cong K_W/mx\gamma_{\pm}^{1/2} \tag{96}$$

The pH of a solution is therefore expressed as

$$pH = -\log a_{H^+} \cong -\log K_W/mx\gamma_{\pm}^{1/2} \tag{97}$$

In order to calculate the pH of a solution the following steps are required at each temperature. From the values of $\gamma_{\pm}$, K_W, and K_{2A}, the degree of hydrolysis is calculated using Equations (69) to (78). The pH is then calculated using Equation (97).

Recent determinations of K_{2A} for carbonic acid at 25°C. have varied from 4.3 to 5.6 x 10^{-11} (21). Using the above procedure for calculating the pH and both the maximum and minimum values of K_{2A}, the calculated pH of a 0.1 m solution was 11.28 and 11.32 at 25°C. Martin (22) reported the pH of a solution of equal concentration at 25°C. to be 11.30. The calculated values of pH are in excellent agreement with the measured pH at 0.1 m. To determine the effect of the activities on the calculated pH values, the pH was also calculated assuming that the activity coefficients were unity. The calculated pH values were then 11.62 and 11.66. The use of concentration rather than activities in the above calculations introduces considerable errors in the results.

A final indication of the reliability at 25°C. may be obtained by considering the activity coefficients of the individual ions in dilute solutions. The sodium compounds may be separated into two groups: (1) those compounds in which the anions are simple such as Cl^-, OH^-, etc. and (2) those compounds in which the anions are polyatomic such as NO_3^-, ClO_4^-, SO_4^-, etc. From a survey of activity coefficient data of sodium compounds (5), the sodium ion activity coefficients were calculated at an ional concentration of 0.6 (0.1 m Na_2CO_3).

TABLE XIV

COMPARISON OF THE SODIUM ION ACTIVITY COEFFICIENTS IN VARIOUS SOLUTIONS AT CONSTANT IONAL CONCENTRATION

Compound	γ_{Na^+} (25°C.)
NaOH	0.708
NaF	0.676
NaCl	0.710
NaBr	0.719
NaI	0.735
$NaClO_3$	0.688
$NaClO_4$	0.701
$NaBr_3$	0.657
$NaNO_3$	0.666
NaOAc	0.744
Na p-toluenesulfonate	0.674
NaCNS	0.731
NaH_2PO_4	0.629
Na_2SO_4	0.667
Na_2CrO_4	0.681
$Na_2S_2O_3$	0.676
Na_2Fumarate	0.682
Na_2Maleate	0.656
Na_2CO_3 (this study)	0.682

The values shown in Table XIV are only approximately correct because of the effect of the anions on the mean activity coefficient. However, the activity coefficient of the sodium ion in sodium carbonate is consistent with most of the sodium compounds with polyatomic anions.

RELIABILITY OF ACTIVITY COEFFICIENT DATA FROM 15 TO 95°C.

Since thermodynamic studies on the behavior of electrolytes over a wide range of temperature have been carried out for only a very few

compounds, it is impossible to judge the reliability of the derived data in relation to data obtained for similar compounds. However, considerations of the experimental limitations, internal consistency of the derived data, and trends indicated from other studies are helpful.

As mentioned previously, the behavior of the concentration cells over the entire temperature range was satisfactory except for the 1.0 and 1.5 m solutions at 50 and 65°C. The e.m.f. at various temperatures was reproducible whether determined during a series at ascending or descending temperatures. Since the rapid temperature equilibration of the cells was established for the low concentrations, the experimental procedure for determining the e.m.f. of the cells at high concentration appears to be justified. The e.m.f. of the 1.0 and 1.5 m concentration cells at 50 and 65°C. were least reliable, but these values had little or no effect on the extrapolation of the data to infinite dilution.

The determination of activity coefficient data from vapor pressure measurements is inherently less accurate than the concentration cell method for several reasons. The ratios of the activity coefficients are not obtained by independent measurements but from the integration of a function dependent upon experimental data, and the errors are accumulative. From 65 to 95°C. the vapor pressure data should be

accurate to 0.01 to 0.1% in order to avoid significant errors in the integration process. In this study the estimated accuracy of the data was roughly 0.2 to 0.5%. However, the errors were minimized by averaging the data by graphical means. Another disadvantage of the vapor pressure method of evaluation for hydrolyzed salts is due to the fact that the activity of the water is a function of the concentration of all the ions in solution and not the concentration of the unhydrolyzed ions of the sodium carbonate as expressed by Equation (90). The errors due to this discrepancy are believed to be small because of the experimental conditions. In addition, the changes in the degree of hydrolysis over the experimental concentration range are small up to 50°C., the highest temperature at which ionization constant data are available.

It is necessary to consider the internal consistency of the derived data in respect to concentration at constant temperature and in respect to temperature at constant concentration. For the former, reference is made to Tables VIII, X, and XII comparing activity coefficients obtained from the experimental measurements and those calculated by the Debye-Hückel equation over the applicable concentration range. Discrepancies in the individual results would be indicated by the inability of the equation to represent the experimentally determined value. Since the agreement between the activity coefficients calculated by both means is excellent at each temperature from 15 to 95°C. over a concentration range of 0.1 m to 1.0 m, there are no apparent inconsistencies in the data at constant temperature.

The activity coefficient data are represented graphically in Figures 10, 11, and 12. Comparison of the results at 65°C. from the two independent methods furnishes a good indication of the reliability of the results in general. At 0.1 m the difference in the activity coefficients is 0.007 or about 1.3%; at 1.0 m the difference in the values is 0.005 or about 1.5%. Considering all the factors involved in the calculation of the data by the two methods, the precision of the results is very satisfactory. It is possible that at any other temperature the activity coefficients are consistently high or low due to accumulative errors in extrapolation. However, from Figure 12 such errors are not apparent.

Sodium hydroxide (23) and sodium sulfate (24) are the only compounds studied over a range of temperatures which would be expected to behave in a manner somewhat analogous to that of sodium carbonate. Over comparable concentration ranges the activity coefficients of both compounds reach maximum values at 25 to 35°C. and then diminish at higher temperatures. For sodium carbonate the maximum values are reached at 50 to 55°C.

It is not possible to make any valid interpretations of the changes in activity coefficients with temperature because of our inadequate fundamental understanding of electrolytic solutions. Obviously the behavior of the electrolytes in solution depends on the relationship of

the attractive forces between ions of the electrolyte and the attractive forces between the individual ions and the solvent. From the Debye-Hückel constant A, the apparent diameter of the ions or the minimum distance of approach of two ions may be calculated.

$$\mathring{a} = A(DT)^{1/2}/35.57 \qquad (55)$$

Temperature, °C.	$\mathring{a}$
15	3.15
25	3.77
37.5	5.29
50	6.36
65	7.09, 6.74*
80	6.09*
95	4.87*

*From vapor pressure data

The above values of $\mathring{a}$ indicate a possible change in the hydration of the ions or a change in ionic association. It is possible that such ions as $(NaCO_3)^-$ exist in the solutions at varying concentrations over the experimental temperature range and account for some of the changes in the activity coefficient data.

From a careful consideration of all the factors, it appears that the activity coefficient data over the entire temperature range are reasonably accurate.

THE RELATIVE PARTIAL MOLAL ENTHALPIES

Since the relative partial molal enthalpies of sodium carbonate in solution are derived directly from the activity coefficient data,

there is little more that can be said concerning their evaluation. Even from the most reliable activity coefficient data, the expected error in the value of $\bar{L}_2$ is not less than ±25 cal./mole. From the data in Table XIII it is possible to draw smooth curves through the values of $\bar{L}_2$ plotted as a function of concentration, which indicates no major discrepancies in the derived data.

Although the values of $\bar{L}_2$ are not highly accurate, it appears that the data are more reliable than that obtained from previous thermochemical measurements (11). The change in the logarithm of the activity coefficient calculated at 18°C. from the thermochemical data at 1.5 m is 0.022/°C. This value corresponds to a slope more than four times that shown at 25°C. in Figure 12. If the activity coefficient at 25°C. and 1.5 m is correct, the change in activity coefficient in 10°C. would be about 35%. Such a radical change in the activity coefficient appears to be very improbable. Further inspection of the data by Bichowsky and Rossini reveals that the heat of dilution values for sodium carbonate are almost double the values of any other sodium compound for comparable concentration differences. It is therefore apparent that thermochemical measurements on sodium carbonate solutions using recent developments in multijunction thermocouples and adiabatic calorimeters are necessary to obtain accurate values of $\bar{L}_2$.

SIGNIFICANCE OF THIS THERMODYNAMIC STUDY

The thermodynamics of sodium carbonate in solution has been studied over a wide range of conditions. It appears that no previous study has used two experimental techniques to obtain data over such a wide temperature range. However, no matter how comprehensive the data may be, the work has little significance unless the results are fully utilized.

There are a number of direct applications for these data. One of the most important is the use of sodium carbonate activities in solution studies. In the calculation of equilibrium constants and reaction kinetics, it is necessary to use the activities of the components of a system. Previously, concentrations of sodium carbonate were generally used as the best approximation of the activities, and inaccuracies in the calculations therefore resulted. In future studies using the activity data, the calculations will be much more reliable.

Although data have been obtained only for pure sodium carbonate in solution and not in mixtures with other electrolytes, the activity of sodium carbonate in any solution may be estimated on the basis of the total ional concentration or the ionic strength (4,5). A typical example of a study in which the data are applicable is the determination of the equilibrium of sodium carbonate, sodium bicarbonate, and carbon

dioxide at various values of pH and temperature. In regard to reaction kinetics, a very important industrial application is the study of the absorption of sulfur dioxide or other gases by sodium carbonate solutions with subsequent chemical reaction.

In many instances, in the pulp and paper industry, sodium carbonate is in solution with other compounds such as sodium sulfide, sodium sulfate, sodium hydroxide, etc. It is necessary to estimate the activities of other compounds as well as the activity of sodium carbonate for each solution at a specified temperature. However, comprehensive data are not available for most of the other compoumds, and their activities must be estimated from the behavior of salts of similar valence type. The reliability of such estimations may be indicated by surveying the available activity coefficient data for compounds at 25°C. (5). For all the compounds of valence type (1-2), similar to sodium carbonate, the solutions are uniform in their behavior. As a first approximation, the activity coefficients of sodium carbonate may be considered to be representative of those of all the (1-2) electrolytes up to 4.0 m. It appears that at other temperatures the activity coefficients of (1-2) salts may be estimated from the sodium carbonate data with reasonable accuracy. However, the behavior of solutions of other valence type compounds is quite variant, and the estimations of activity from available data are less reliable.

Another use of the thermodynamic data is the prediction of the behavior of sodium carbonate solutions at high temperature. As outlined previously, it is possible to calculate the pH of a solution from $\gamma_{\pm}$, K_W, and K_{2A}. However, the second ionization constant of carbonic acid has been determined only up to 50°C., and values at higher temperatures must be estimated by extrapolation. In addition, the ionization constant of water has not been determined with accuracy at high temperatures. The calculated pH values above 50°C. must therefore be considered only as rough approximations.

As mentioned previously, thermochemical measurements using modern techniques are necessary for a more complete understanding of sodium carbonate solutions. However, in the calculation of the integral heat of dilution data, suitable corrections are necessary to account for the heat effects due to hydrolysis. The results from this study should therefore be helpful in interpreting the experimental measurements of future studies.

In conclusion, it should be emphasized that our understanding of solution behavior may be broadened only by the accumulation and interpretation of thermodynamic and thermochemical data for many electrolytic solutions. In this respect it is felt that the results of this work represent a significant contribution to our comprehension of solution behavior.

SUMMARY AND CONCLUSIONS

1. The e.m.f. of concentration cells without liquid junction were measured at 25°C., and the reversibility of the proposed cell reactions was established using independent activity coefficient data and fundamental thermodynamic equations. The e.m.f. measurements were subsequently extended from 15 to 65°C. at concentrations from 0.1 m to 1.5 m.

2. The vapor pressures of sodium carbonate solutions from 0.1 m to 2.5 m were determined at 65 to 95°C. using the gas saturation method. The estimated maximum errors in the results were 0.2 to 0.5%.

3. The activity coefficients at 15 to 65°C. were calculated from the concentration cell data. The Debye-Hückel equation was used to extrapolate the experimental data to infinite dilution. From the vapor pressure determinations at 65 to 95°C. the logarithmic ratios of the activity coefficients were evaluated by integration of the Gibbs-Duhem equation from $m_1 = 0.4m$ to m_2. Calculation of the absolute values of the activity coefficients was accomplished by employing the Debye-Hückel equation. The reliability of results at 25°C. was established by (1) comparison with previously published data, (2) calculation of the pH of a 0.1 m solution, and (3) comparison of the sodium ion activity coefficient of sodium carbonate with those of similar sodium compounds. From a careful consideration of the possible

errors introduced by the experimental techniques, methods of evaluation of the experimental data, internal consistency of the derived data, and the trends in the behavior of similar compounds, it was concluded that the results over the entire temperature range were reasonably accurate.

4. The relative partial molal enthalpies of sodium carbonate were calculated at 25 to 80°C. from the activity coefficient data. Although the results were not highly accurate, the results appeared to be more reliable than the values of $\overline{L}_2$ calculated from available thermochemical measurements.

5. The significance of the data was discussed in respect to applications in studies of equilibria and reaction kinetics, prediction of the activity of sodium carbonate and similar compounds in mixed solutions, estimation of pH values of sodium carbonate solutions at high temperature, and application in thermochemical studies. It was concluded that the work represented a significant contribution to our understanding of solution behavior.

LITERATURE CITED

1. Lortie, Leon, and Demers, Pierre, Can. J. Research 18B:373-385 (1940).

2. Saegusa, Fumihiko, Science Repts. Tokohu Univ. First Ser. 34:147-152 (1950).

3. Chem. Eng. 60, no. 3: 193 (March 1953).

4. Lewis, Gilbert N., and Randall, Merle. Thermodynamics and the free energy of chemical substances. New York, McGraw-Hill Book Co., 1923. 623 p.

5. Harned, Herbert S., and Owen, Benton B. The physical chemistry of electrolytic solutions. 2d ed. New York, Reinhold, 1950. 621 p.

6. The collected works of J. Willard Gibbs. Vol. 1, p. 55-354. New York, Longmans, Green and Co., 1928. 434 p.

7. Debye, Peter, and Hückel, Emil, Physik. Z. 24:185-206 (1923).

8. Jones, Grinnell, and Dole, Malcolm, J. Am. Chem. Soc. 51:1072-1091, especially 1084-1085 (1929).

9. Harned, Herbert S., and Owen, Benton B. The physical chemistry of electrolytic solutions. 2d ed. Especially p. 361. New York, Reinhold, 1950. 621 p.

10. Watson, K. N., and Kowalke, O. L., Ind. Eng. Chem. 22:370-376 (1930).

11. Bichowsky, F. Russell, and Rossini, Fredrick D. The thermochemistry of the chemical substances. Especially p. 144. New York, Reinhold, 1936. 460 p.

12. Kobe, Kenneth A., and Sheehy, Thomas A., Ind. Eng. Chem. 40:99-102 (1923).

13. Foulk, C. W., and Hollingsworth, Marion, J. Am. Chem. Soc. 45:1220-1228 (1923).

14. Harned, Herbert S., J. Am. Chem. Soc. 51:416-427 (1929).

15. Demers, Pierre, Can. J. Research 17A:77-81 (1939).

16. International Critical Tables. Vol. 3, p. 82-83, New York, McGraw-Hill Book Co., 1926.

17. Lange, Norbert Adolph. Handbook of chemistry. 8th ed. p. 1219-1220. Sandusky, Ohio, Handbook Publishers, 1952.

18. Pearce, J. N., and Snow, R. D., J. Phys. Chem. 31:231-245 (1927).

19. Lange, Norbert Adolph. Handbook of chemistry. 8th ed. p. 1507. Sandusky, Ohio, Handbook Publishers, 1952.

20. Harned, Herbert S., and Owen, Benton B. The physical chemistry of electrolytic solutions. 2d ed. Especially p. 119. New York, Reinhold, 1950. 621 p.

21. Harned, Herbert S., and Scholes, Samuel R., J. Am. Chem. Soc. 63:1706-1709 (1940).

22. Martin, George E. The hydrolysis of sodium sulfide in mixtures with sodium hydroxide. Doctor's dissertation. Especially p. 53. Appleton, Wis., The Institute of Paper Chemistry, 1948. 88 p.

23. Harned, Herbert S., and Hecker, John C., J. Am. Chem. Soc. 55:4838-4849 (1933).

24. Harned, Herbert S., and Hecker, John C., J. Am. Chem. Soc. 56:650-653 (1934).

APPENDIX

SAMPLE CALCULATIONS

Activity Coefficients at 25°C. From E.M.F. Measurements

Concentration cell: 0.1 m-0.2 m

$m_r = 0.1007$

$m_2 = 0.2005$

$E(obs.) = -20.26$ mv.

$S_f = 0.7164$

$c_r = 1000\ mP/(mM + 1000)$

$= (1000)\ (0.1007)\ (1.0079)/(0.1007)\ (106.0) + 1000$

$= 0.1005 \quad ; \sqrt{r} = 6c = 0.6030$

$c_2 = 0.2000 \quad ; \sqrt{2} = 1.2000$

From the Debye-Hückel Equation (57)

$$\log \gamma_{\pm r} = -S_f \sqrt{\sqrt{r}/(1+A\sqrt{\sqrt{r}})} + Bc_r - \log\ (1+0.054\ m_r)$$

$$= (-0.7164)\ (0.6030)^{1/2}/[1+A(0.6030)^{1/2}]$$

$$+B\ (0.1005) - \log\ [1+0.054\ (0.1007)]$$

$$= -0.5563/(1+0.7765\ A) + 0.1005B-0.00023$$

$$\log \gamma_{\pm 2} = -0.7848/(1+1.0954A) + 0.2000B-0.0047$$

The above calculations are made for each concentration cell. The evaluation of constants A and B is carried out using Equations (59) through (65). Assume A = 0.88 and B = 0.02. From Equation (59)

$$E(\text{calc.}) = -88.725(\log m_2/m_r + \log \gamma_{\pm 2} - \log \gamma_{\pm r}$$

$$= -88.725 \left[\log 0.2005/0.1007 + \left(\frac{-0.7848}{1-0.88(1.0954)} + (0.2000)\ (0.02)\ -0.0047\right)\right.$$

$$\left. - \left(\frac{-0.5563}{1-0.88(0.7765)} + (0.1005)\ (0.02)\ -0.0023\right)\right] = -20.36$$

$$\Delta E = (-20.26)-(-20.36) = +0.10$$

From Equation (63)

$$\Delta E = -88.725 \left[S_f \sqrt{2}/(1+A\sqrt{\sqrt{2}})^2 - S_f \sqrt{r}/(1-A\sqrt{\sqrt{r}})^2\right] \Delta A - (88.725)\ (c_2-c_r)\ \Delta B$$

$$\Delta E = +0.10 = -88.725 \left[\left(\frac{(0.7164)(1.2000)}{[1+0.88(1.0954)]^2} - \frac{(0.7164)(0.6030)}{[1+0.88(0.7765)]^2}\right) \Delta A - (0.2000-0.1005)\ \Delta B\right] ; \quad -0.10 = 88.725(0.0700\ \Delta A - 0.995\ \Delta B)$$

A series of five equations like the above are calculated for each of the concentration cells from m_2 0.2 to m_2 1.0. ΔA and ΔB are solved by the method of averages

$$\Delta A = -0.0029 \qquad A' = 0.877$$

$$\Delta B = -0.018 \qquad B' = 0.002$$

The above process is repeated until ΔA, ΔB, and ΔE are negligible. The final values are

$$A = 0.878$$

$$B = 0.001$$

$\gamma_{\pm r}$ is calculated by the Debye-Hückel equation.

$$\log \gamma_{\pm r} = -0.5563/[1+(0.878)(0.7765)] - 0.001\ (0.1005) - 0.0023$$

$$= -0.3328$$

$$\gamma_{\pm r} = 0.465$$

$\gamma_{\pm 2}$ is calculated from Equation (83)

$$\log \gamma_{\pm 2} = -E/88.725 - \log m_2/m_1 - \log \gamma_{\pm r}$$

$$= -(-20.26/88.725) - \log 0.2005/0.1007 - \log 0.465$$

$$\gamma_{\pm 2} = 0.393$$

Activity Coefficients Calculated From Vapor Pressures

Temperature : 80°C.

Reference solution : 0.4000 m

Vapor pressure @ 0.4000 m = 349.15

Vapor pressure @ 0.8000 m = 344.35

At 0.4 m, $\log a_1 = \log P_1/P = \log 349.15/355.30$

$$= -0.00758$$

At 0.8 m, $\log a_1 = 0.01359$

From Equation (58)

$$\log (\gamma_{\pm 2}/\gamma_{\pm r}) = -(18.502/m)\ d \log a_1 - \log(m_2/m_r)$$

By graphical integration from m_r to m_2

$$\int (18.502/m)\ d \log a_1 = -0.19544$$

$$\log (\gamma_{\pm 2}/\gamma_{\pm r}) = -(-0.19544) - \log (0.8/0.4) = -0.10559$$

$$D \equiv \log(f_{\pm 2}/f_{\pm r}) = \log(\gamma_{\pm 2}/\gamma_{\pm r}) + \log(1-0.054\ m_2) - \log (1-0.054\ m_r)$$

$$= -0.10559 - 0.00909 = -0.09650$$

Assume A = 1.45 and B = -0.150. From Equation (86)

$$D\ (\text{calc.}) = [-S_f\sqrt{I^2}/(1+A\sqrt{I^2}) + Bc_2]-[-S_f\sqrt{I^r}/(1+A\sqrt{I^r})+Bc_r]$$

$$= \{(-0.8166)(4.6440)^{1/2}/[1+1.45(4.6440)^{1/2}]$$
$$+(-0.150)(0.7740)\} - \left[\frac{-0.8166(2.3286)^{1/2}}{1-1.45(2.3286)^{1/2}}\right.$$

$$\left.+(-0.150)(0.3881)\right] = -0.0954$$

$$\Delta D = (-0965)-(-0.0954) = -0.0011$$

From Equation (87)

$$\Delta D = [3.7923/(4.1248)^2-2.3758/(3.2127)^2]\ \Delta A$$
$$+ (0.7740-0.3881)\ \Delta B$$

$$\Delta D = -0.0011 = 0.0387\,\Delta A + 0.3859\ \Delta B$$

From a series of nine equations from $m_2 = 0.1$ to $m_2 = 1.0$, ΔA and ΔB are solved by the method of averages. The process is repeated and the final values are

$$A = 1.480$$

$$B = -0.153$$

From the Debye-Hückel equation

$$\log \gamma_{\pm r} = -0.3824-0.0594-0.0093 = -0.4511$$

$$\gamma_{\pm r} = 0.354$$

From the above calculated ratio of activity coefficients,

$$\log \gamma_{\pm 2} = -0.1056 -(-0.4511)$$

$$= -0.5567$$

$$\gamma_{\pm 2} = 0.278$$

Errors Due to Hydrolysis

Temperature 50°C.

$K_W = 5.474 \times 10^{-14}$

$K_{2A} = 6.73 \times 10^{-11}$

$\gamma_{\pm\ 0.1} = 0.524$; $\gamma_{CO_3^{=}} = 0.275$

$\gamma_{\pm 1.0} = 0.316$; $\gamma_{CO_3^{=}} = 0.0999$

$K_H = K_W/K_{2A} = 5.474 \times 10^{-14}/6.73 \times 10^{-11}$

$= 8.134 \times 10^{-14}$

At 0.1 m

$k_H = K_H\ (\gamma_{CO_3^{=}}/\gamma_{HCO_3^-}\ \gamma_{OH^-}) = 8.134 \times 10^{-4}(0.275/0.524)$

$= 4.269 \times 10^{-4}$

$k_H = mx^2/m(1-x)$

$x = 0.0632$

$m_{\pm 0.1} = \left\{[2(0.1)]^2\ [1(0.1-0.0632)]\right\}^{1/3}$

$= [(0.04)(0.0936)]^{1/3}$

At m = 1.0,

$k_H = 8.134 \times 10^{-4}\ (0.0999/0.316) = 2.572 \times 10^{-4}$

$x = 0.0506$

$m_{\pm 1.0} = \left\{[2(1.0)]^2\ [1(1-.0506)]\right\}^{1/3}$

$(4)(0.949)$

$$m_{\pm 1.0}/m_{\pm 0.1} = [(4)(0.949)/(0.04)(0.0936)]^{1/3}$$
$$= 10.06$$

$m_{\pm 1.0}/m_{\pm 0.1}$ (uncorrected) = 10.00

error = (10.06-10.00)(100)/10.00 = 0.6%

Vapor Pressure Determinations

From Equation (81)

$$P_1 = w_1 \underline{P}_1 P/w(\underline{P}-P) + w_1 P$$

Concentration: 1.146 m

Temperature: 65°C.

w = water vapor removed from water cells = 0.7660 g.

w_1 = water vapor removed from solution cells = 0.7660 g.

Barometric pressure = Reading -scale correction

- Temp. corr. = 740.0 @ 20 C. -1.0 - 2.4 = 736.6 mm. Hg.

$\Delta \underline{P}$ = 10.4 cm. water = 7.6 mm. Hg

$\underline{P}$ = 736.6 + 7.6 = 744.2

$\Delta \underline{P}_1$ = 0.6 cm. water = 0.4 mm. Hg, $\underline{P}_1$ = 737.0 mm. Hg

P = 187.65 mm. Hg

P_1 = (0.7304)(737.0)(187.65)/[(0.7660)(744.2 - 187.6) + (0.7304)(187.65)]
= 179.28 mm. Hg

TABLE XV

ELECTROMOTIVE FORCES OF CONCENTRATION CELLS AT 15 TO 65°C.

Molality	15°	25°	37.5°	50°	60°
0.1005	reference solution		0.0	0.0	0.0
0.2008	-18.3	-19.8	-22.3	-24.0	-25.2
	-18.5	-20.3	-22.4	-24.4	-25.2
	-18.6	-20.3	-22.4	-24.2	-
	-	-20.2	-22.3	-	-
0.4009	-37.1	-40.1	-44.5	-46.6	-48.7
	-37.6	-40.4	-44.8	-47.3	-49.0
0.6014	-48.1	-52.0	-57.1	-60.4	-62.7
	-48.3	-51.9	-58.0	-59.9	-62.4
	-	-52.1	-	-	-
0.8470	-58.5	-62.4	-66.9	-70.5	-72.0
	-57.4	-62.1	-67.2	-70.6	-72.1
	-	-62.0	-	-	-
1.0047	-62.3	-67.6	-71.4	-73.6	-75.5
	-63.2	-66.8	-71.2	-74.7	-76.3
	-	-66.8	-71.7	-74.8	-76.4
1.5355	-72.0	-77.6	-83.0	-86.4	-88.4
	-73.4	-79.0	-84.0	-87.8	-88.8
	-	-78.9	-83.8	-87.4	-88.6
	-	-78.8	-83.9	-	-

TABLE XVI

VAPOR PRESSURES OF SODIUM CARBONATE SOLUTIONS AT 65 TO 95°C.

Molality	Vapor pressure in mm. Hg		
	65°C.	80°C.	95°C.
(water)	187.65	355.3	634.3
0.1009	185.38	353.9	631.9
	185.42	353.9	632.2
	186.50	353.6	631.9
	186.11	353.7	631.5
	185.29	-	-
0.1507	187.26	352.6	630.0
	186.92	352.7	629.7
	186.37	352.5	629.8
	186.39	352.6	630.0
	186.53	-	-
	186.51	-	-
	186.53	-	-
	186.14	-	-
0.1999	187.24	353.0	629.0
	185.97	351.1	628.7
	186.58	351.5	629.0
	187.89	351.1	-
0.4013	182.34	352.7	624.5
	184.14	350.8	624.2
	184.96	349.7	623.9
	184.68	349.3	625.0
0.5017	181.67	347.4	-
	182.54	348.2	-
	182.97	347.9	-
	183.38	-	-
0.5994	177.59	337.3	620.3
	181.60	345.8	618.0
	182.05	346.2	618.9
	181.99	-	619.3

TABLE XVI (CONTINUED)

Molality	Vapor pressure in mm. Hg 65°C.	80°C.	95°C.
0.6934	182.06	-	-
	182.13	-	-
	182.05	-	-
	181.21	-	-
0.8046	181.55	334.3	613.4
	181.61	344.6	614.0
	182.01	344.0	614.1
	-	344.9	614.4
1.001	181.85	343.9	611.6
	181.73	343.9	610.5
	181.32	343.4	610.2
	181.56	343.1	610.2
1.146	179.69	341.4	607.5
	179.28	340.6	607.1
	179.40	340.2	607.1
	178.91	340.5	607.4
1.444	172.68	335.7	605.1
	175.35	334.3	603.8
	175.82	334.0	604.3
	174.77	334.0	603.5
	176.64	-	-
	177.80	-	-
	177.27	-	-
	177.85	-	-
1.519	176.65	335.4	600.4
	177.11	336.1	601.6
	176.75	336.6	600.6
	-	336.8	600.5
2.011	173.42	331.3	589.6
	174.42	330.8	589.3
	173.43	331.0	589.2
	173.96	332.0	590.2
2.520	169.74	323.6	579.3
	169.67	324.4	577.5
	169.91	324.0	578.7
	169.97	323.2	578.2